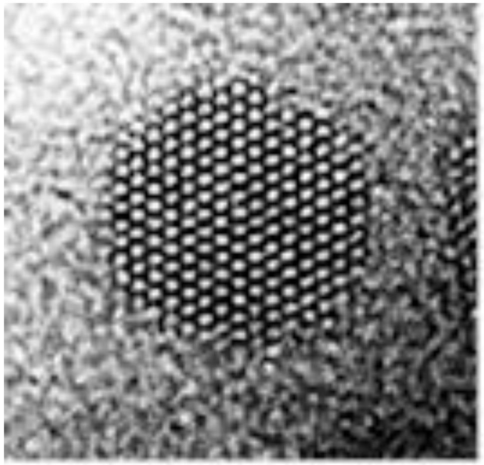
Ab initio Calculations of Optical Properties of Quantum Dots and Wires

Lin-Wang Wang

Computational Research Division
Lawrence Berkeley National Laboratory

US Department of Energy
BES, Office of Science

Semiconductor Nanocrystals



CdSe
quantum dot
TEM image

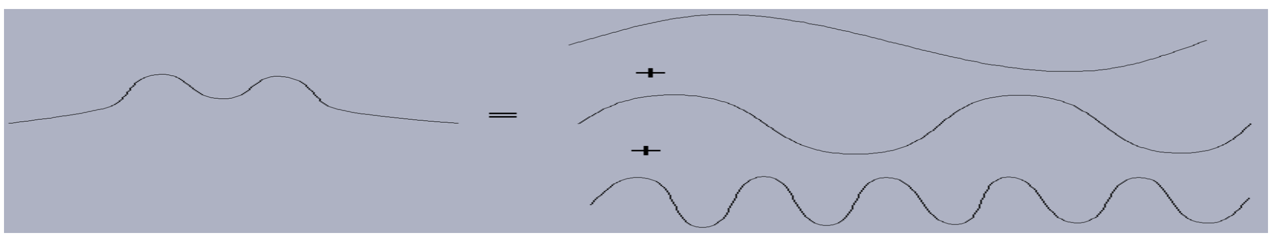
❖ 1,000 ~ 10,000 atoms, too large for direct $O(N^3)$ ab initio calcu

❖ New O(N) computational method is needed

Planewave pseudopotential calculations

$$\left\{-\frac{1}{2}\nabla^2 + V(r)\right\}\psi_i(r) = \varepsilon_i \psi_i(r)$$

$$\psi_i(r) = \sum_q C_i(q) e^{iqr}$$



Fast Fourier Transformation between real space ψ(r) and Fourier space C(q).

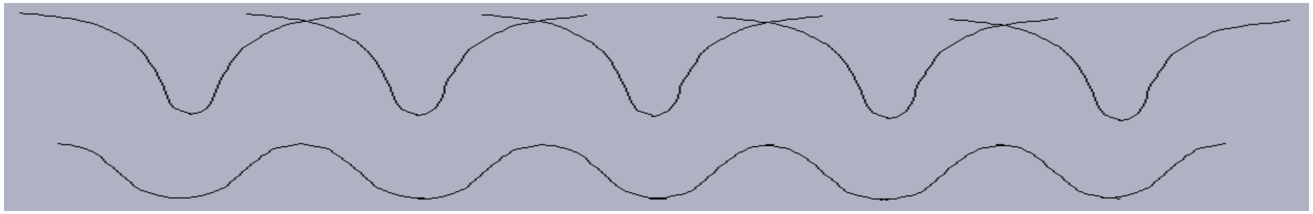
Empirical pseudopotential calculations for nanostructures

Generating potential directly from atomic positions {R}

$$V(r) = \sum_R v_\alpha (r - R)$$

$v_\alpha(r)$

$V(r)$

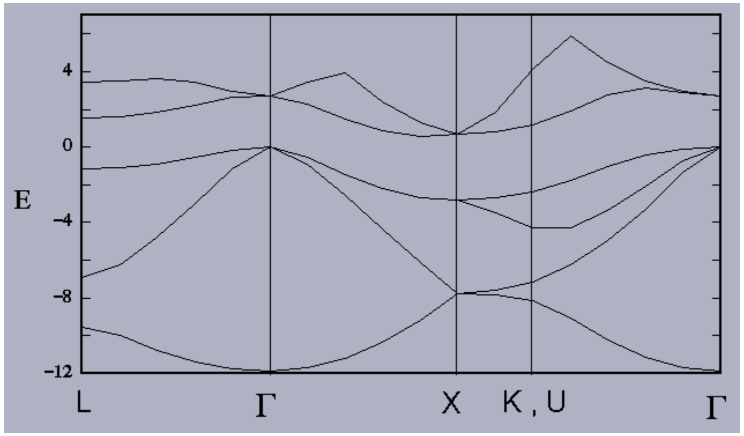


Empirical pseudopotential method (EPM)

Fit $v_\alpha(r)$ from experimental band structures

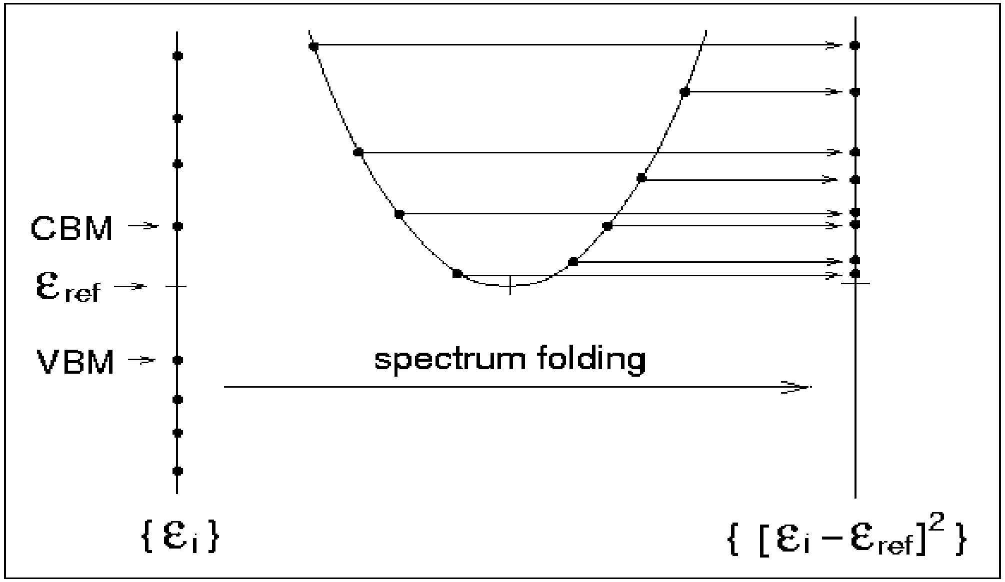
and ab initio V(r).

EPM provides one of the best band structures for semiconductors



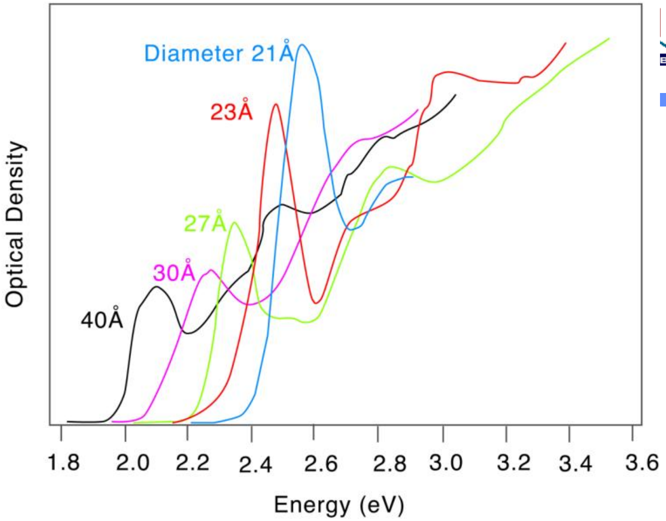
Folded Spectrum Method and Post Processing

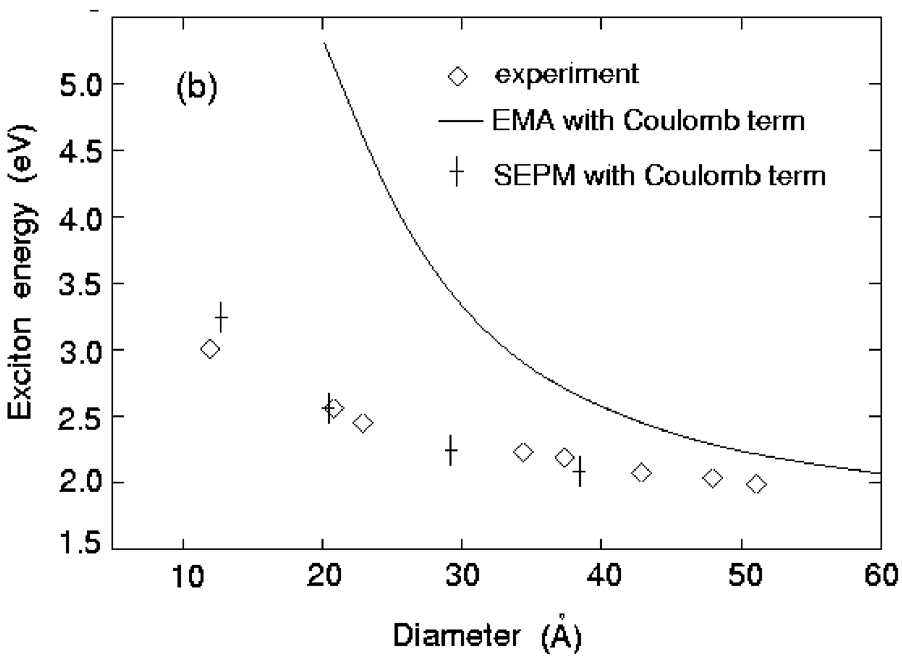
$$H\psi_i = \varepsilon_i \psi_i \qquad (H - \varepsilon_{ref})^2 \psi_i = (\varepsilon_i - \varepsilon_{ref})^2 \psi_i$$

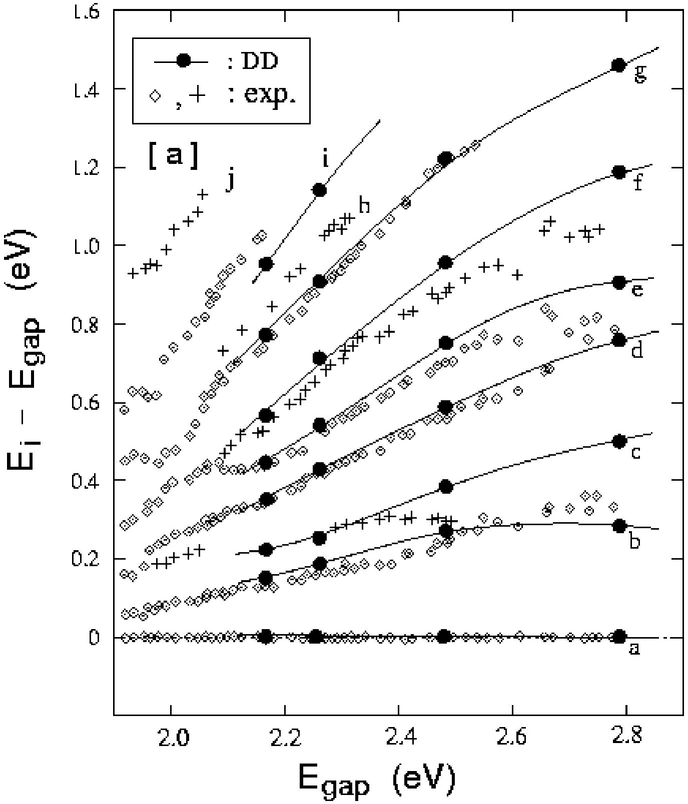


Using $\{\Psi_i, \varepsilon_i\}$ and Coulomb/exchange integral for limited CI calc.
---- many-body effects, optical fine struct., Auger effects, entangle

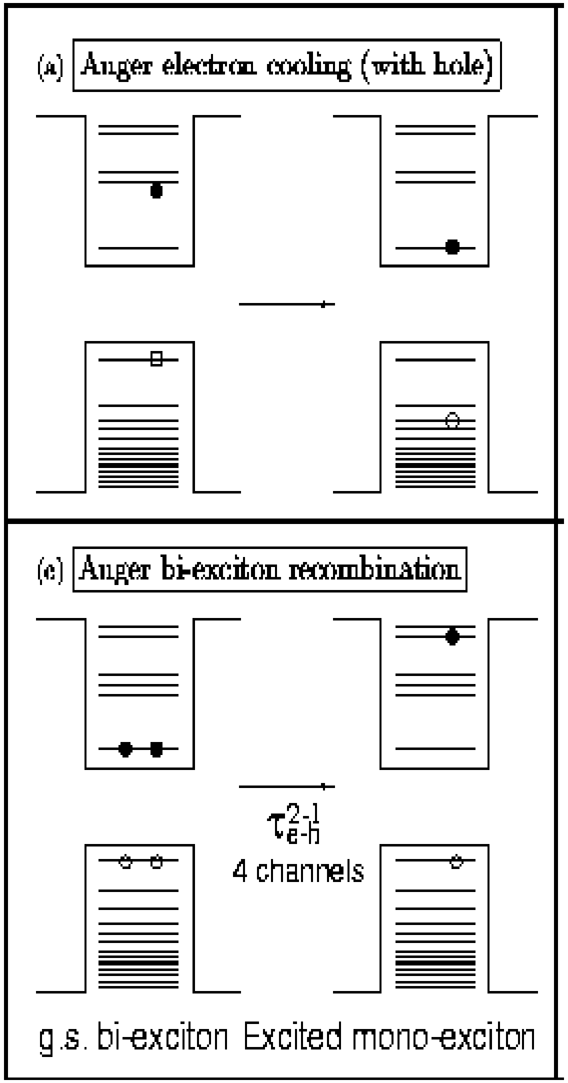
CdSe quantum dot results

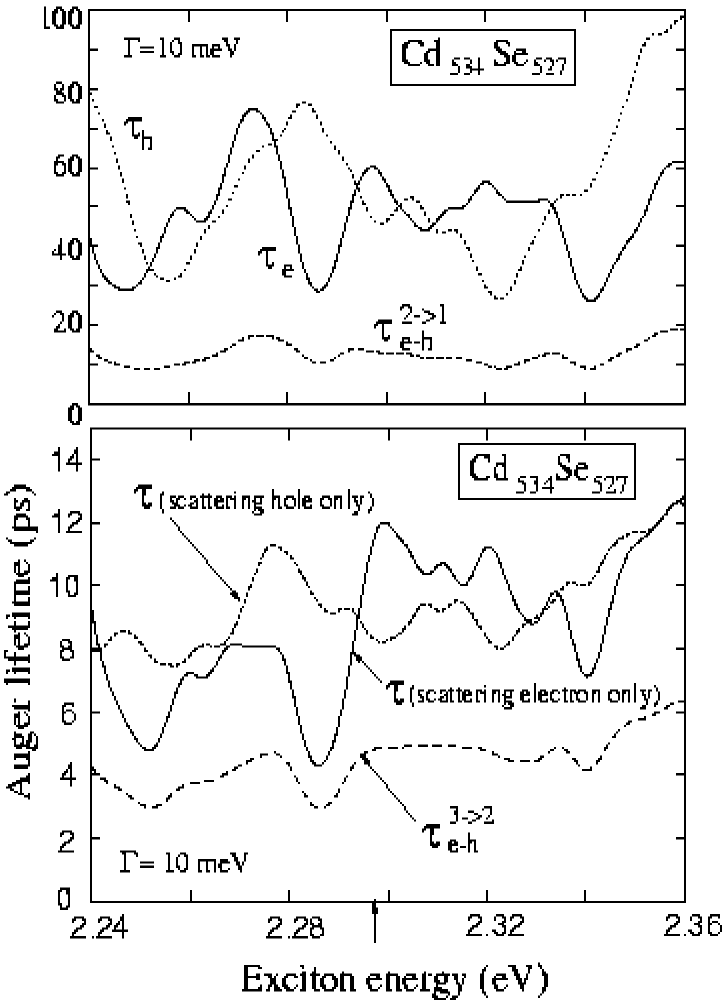






Auger effect in CdSe quantum dot





Auger life times

Exp. Calc.

Cooling

>0.5ps ~0.2–0.5ps

2 exciton–>1 exc.

~2.7 ps ~2. ps

$\tau_{2eh->1eh} / \tau_{3eh->1eh}$

2.7 2.4

Need ab initio elements in the calculation

- ❖ EPM calculation: what you fit is what you get
- ❖ In practice, it is difficult to fit the surface passivation

(1) Direct ab initio calculation is too expensive: $O(N^3)$ scaling

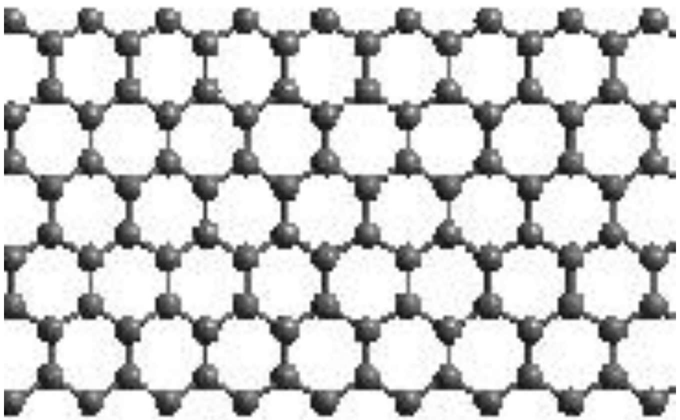
(2) Under DFT (LDA), all we need is $\rho(r)$ [then we can get $V(r)$].

(3) We will use charge patching method to get $\rho(r)$.

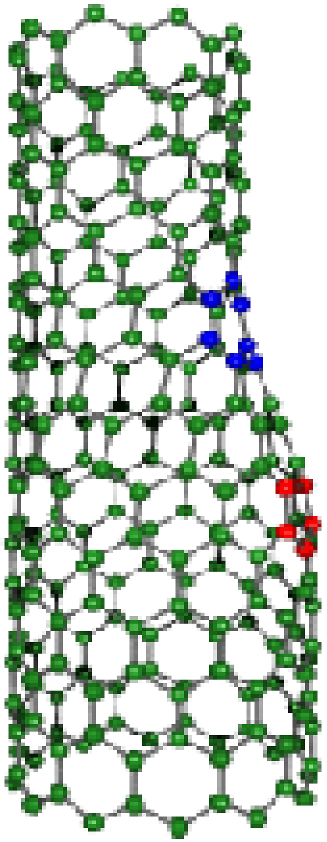
(4) We will use folded spectrum method (FSM) to get $\{\Psi_i, \varepsilon_i\}$.

Charge patching method

Selfconsistent LDA calculation of a single graphite sheet



Non-selfconsistent LDA quality potential for nanotube

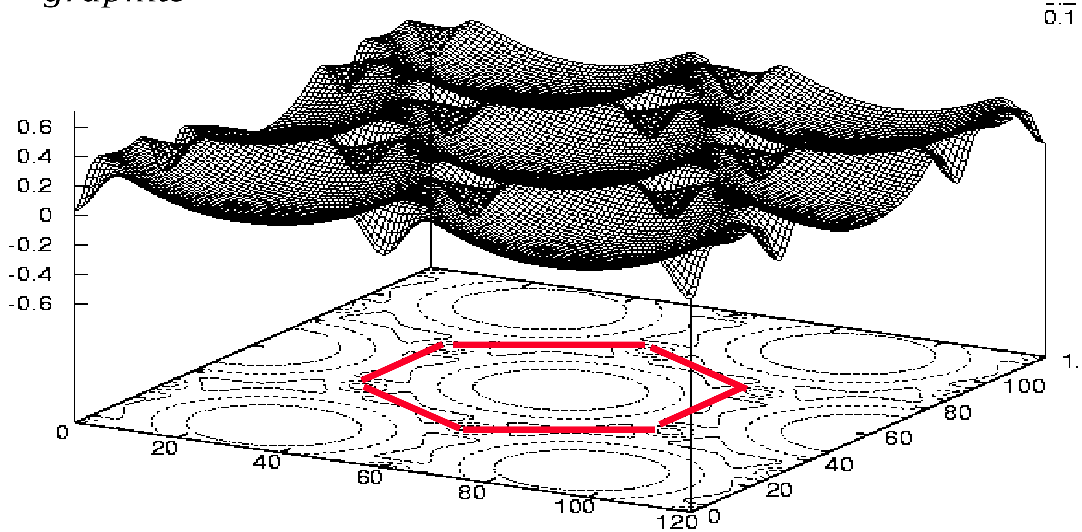


Get information from small system ab initio calc., then generate the charge densities for large systems

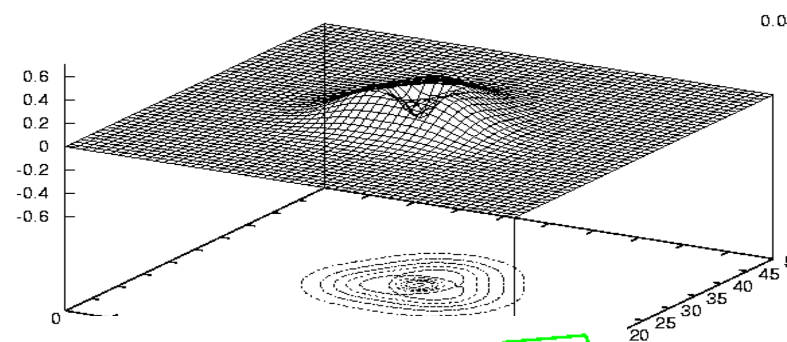
Motif based charge patching method

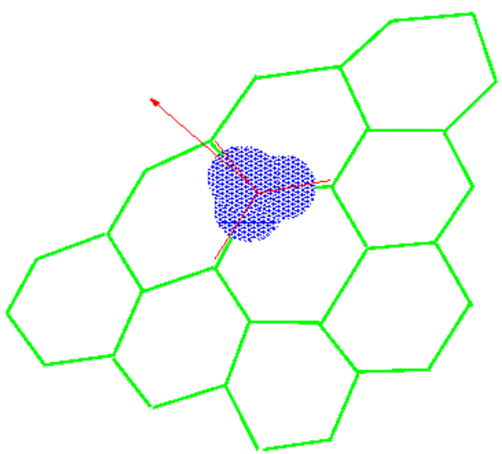
$$\rho_{motif}(r) = \rho_{graphite}(r) \times \frac{\rho_{atom}(r - R_0)}{\sum_R \rho_{atom}(r - R)}$$

$\rho_{graphite}(LDA)$



ρ_{motif}





$$\rho^{patch}_{nanotube}(r) = \sum_R \rho^{aligned}_{motif}(r - R)$$

Error: 1%, ~20 meV eigen energy error.

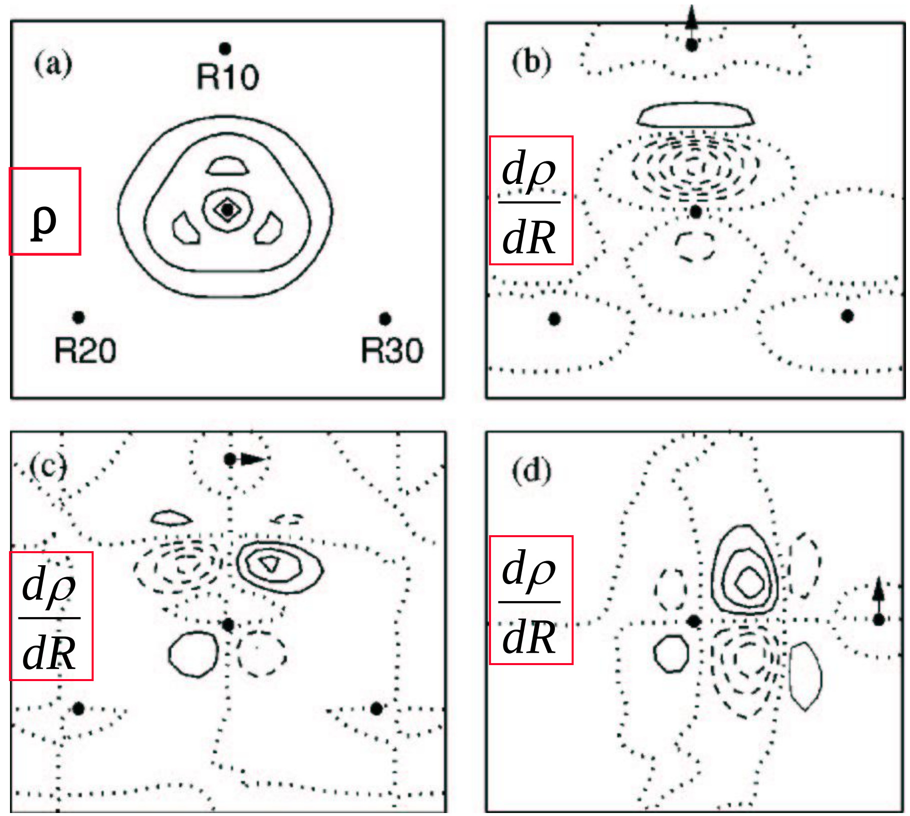
Motif derivatives to the nearest neighbor atom positions

$$\frac{d\rho}{dR} = \{\rho(r)[R1+dR, R2, R3] - \rho(r)[R1, R2, R3]\} / dR$$

$$\rho^{patch}_{nanotube}(r) = \sum_{R} \{\rho^{aligned}_{motif}(r-R) + \frac{d\rho}{dR_j}(r-R) * (R_j - R_j^0)\}$$

The motif charge dependence on the neighboring atom positions has been taken into account.

But how about the long range electric field ?

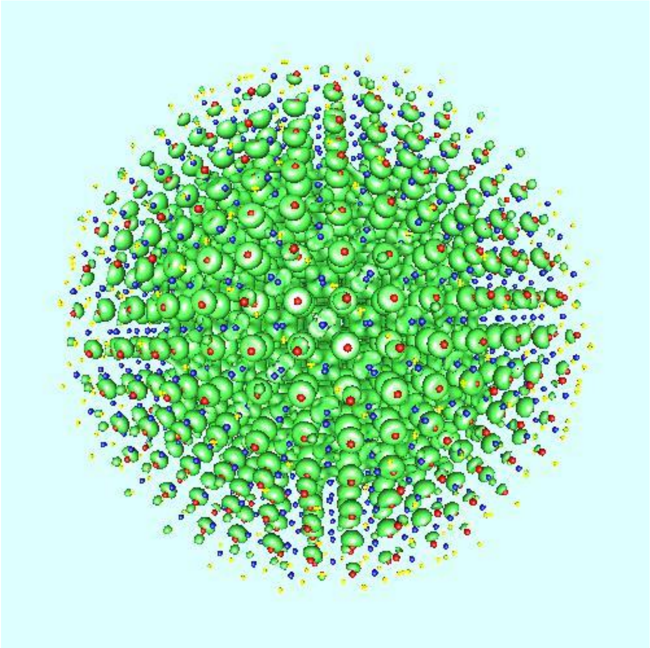


Charge patching: free standing quantum dots

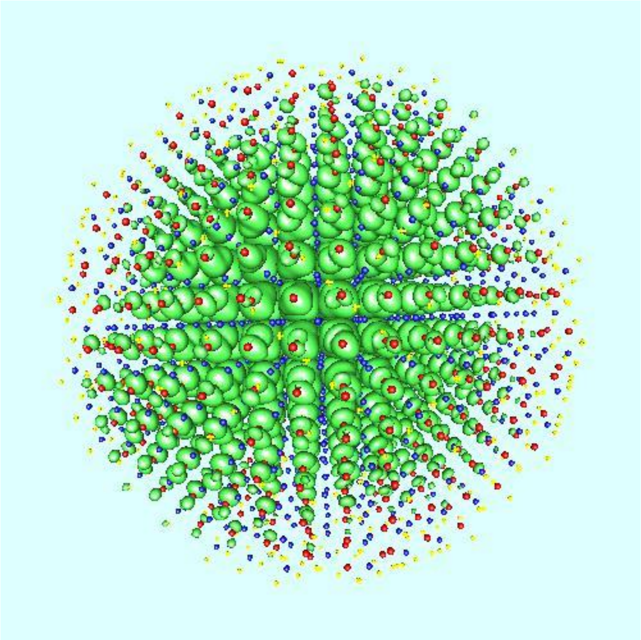
$In_{675}P_{652}$ LDA quality calculations (eigen energy error ~ 20 meV)

64 processors (IBM SP3) for ~ 1 hour

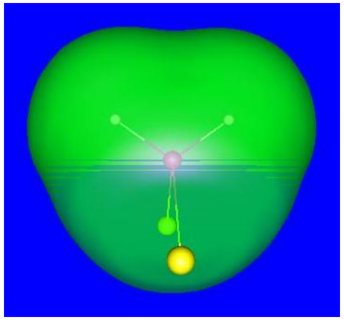
CBM

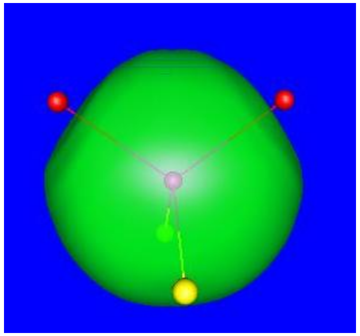


VBM

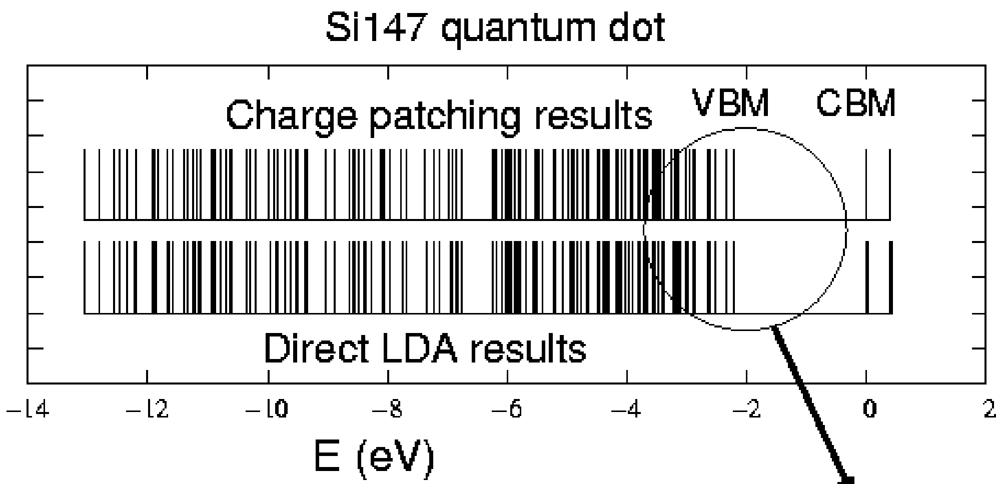


Total charge density motifs



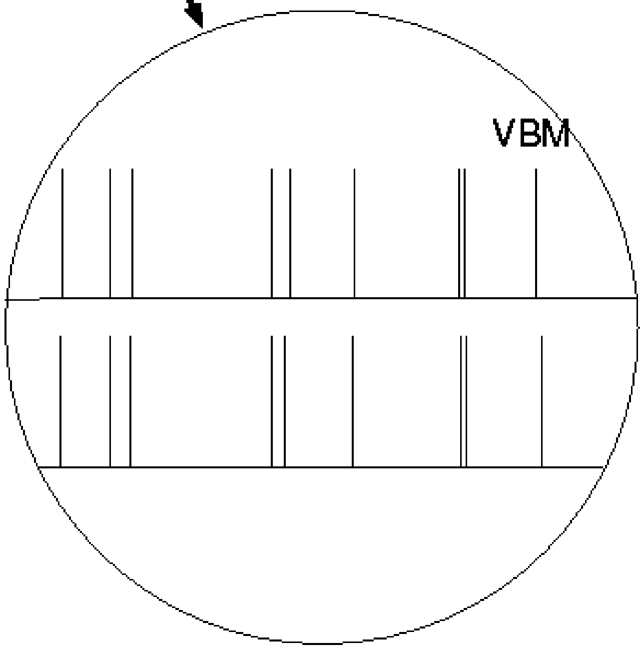


The accuracy for the small Si quantum dot



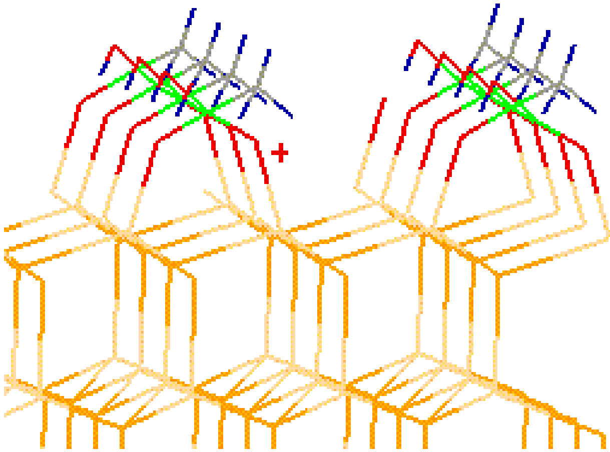
Average E error ~ 5 meV

Max E error ~ 16 meV

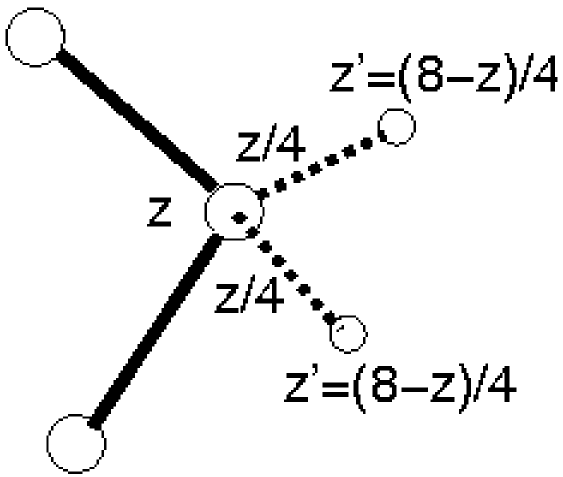


Ideal surface passivation for IV−IV,III−V,II−VI semiconductors

Actual surface passivation can be complicated and experimentally uncertain.



We use ideal (best) passivation
(used to be used in surface calculation).



Pseudohydrogen H:

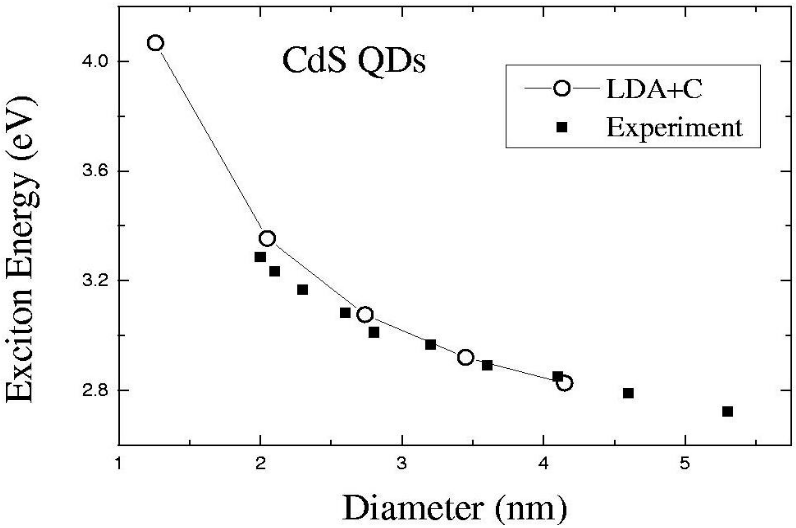
Z	atom
0.5	VI
0.75	V
1.0	IV
1.25	III
1.5	II

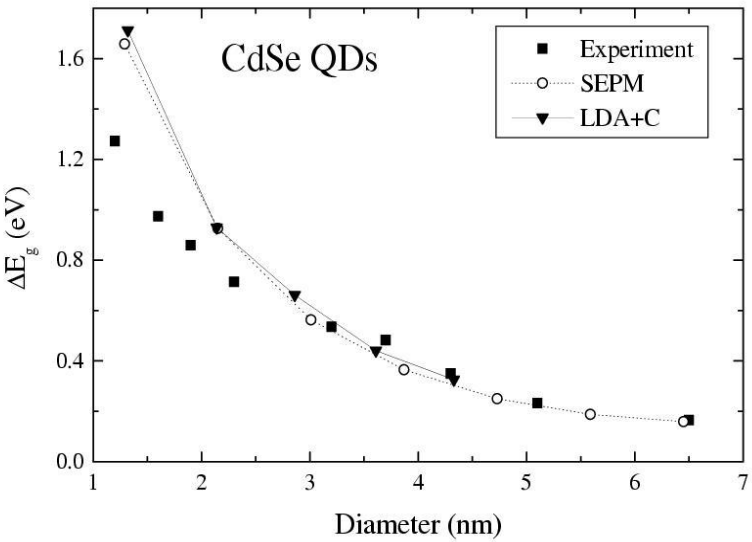
Quantum dot and wire calculations for semiconductor materials

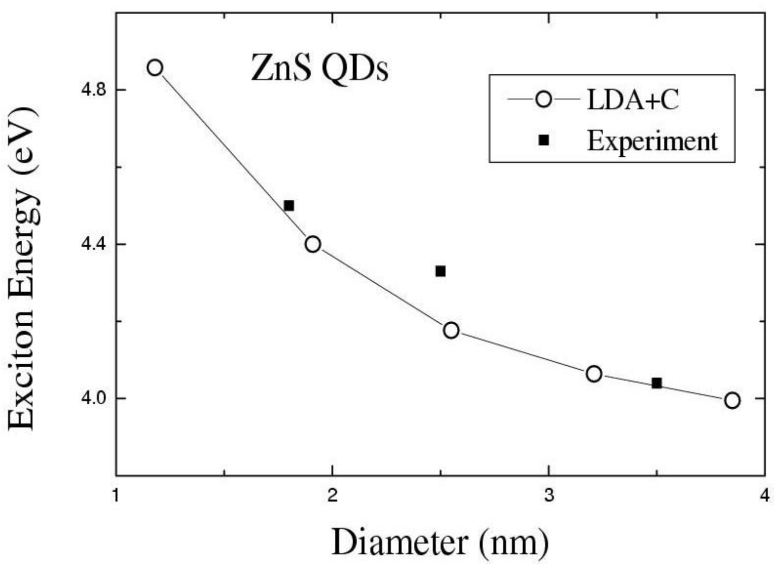
IV-IV: Si

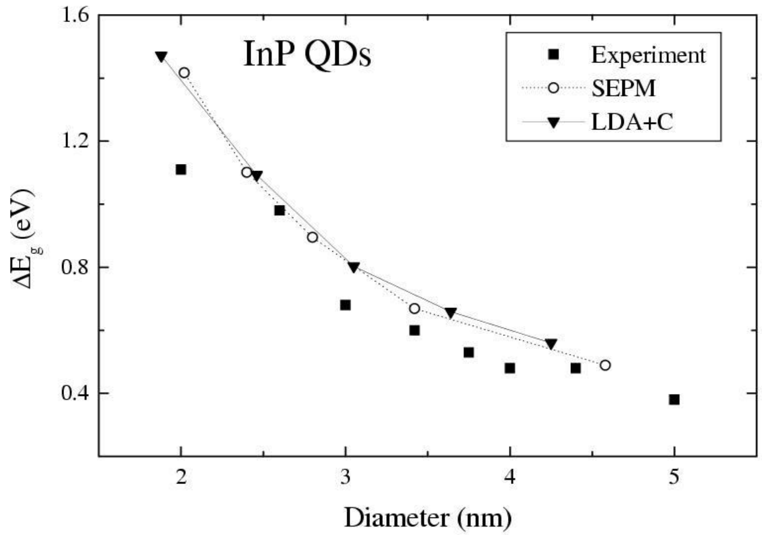
III-V: GaAs, InAs, InP, GaN, AlN, InN

II-VI: CdSe, CdS, CdTe, ZnSe, ZnS, ZnTe, ZnO







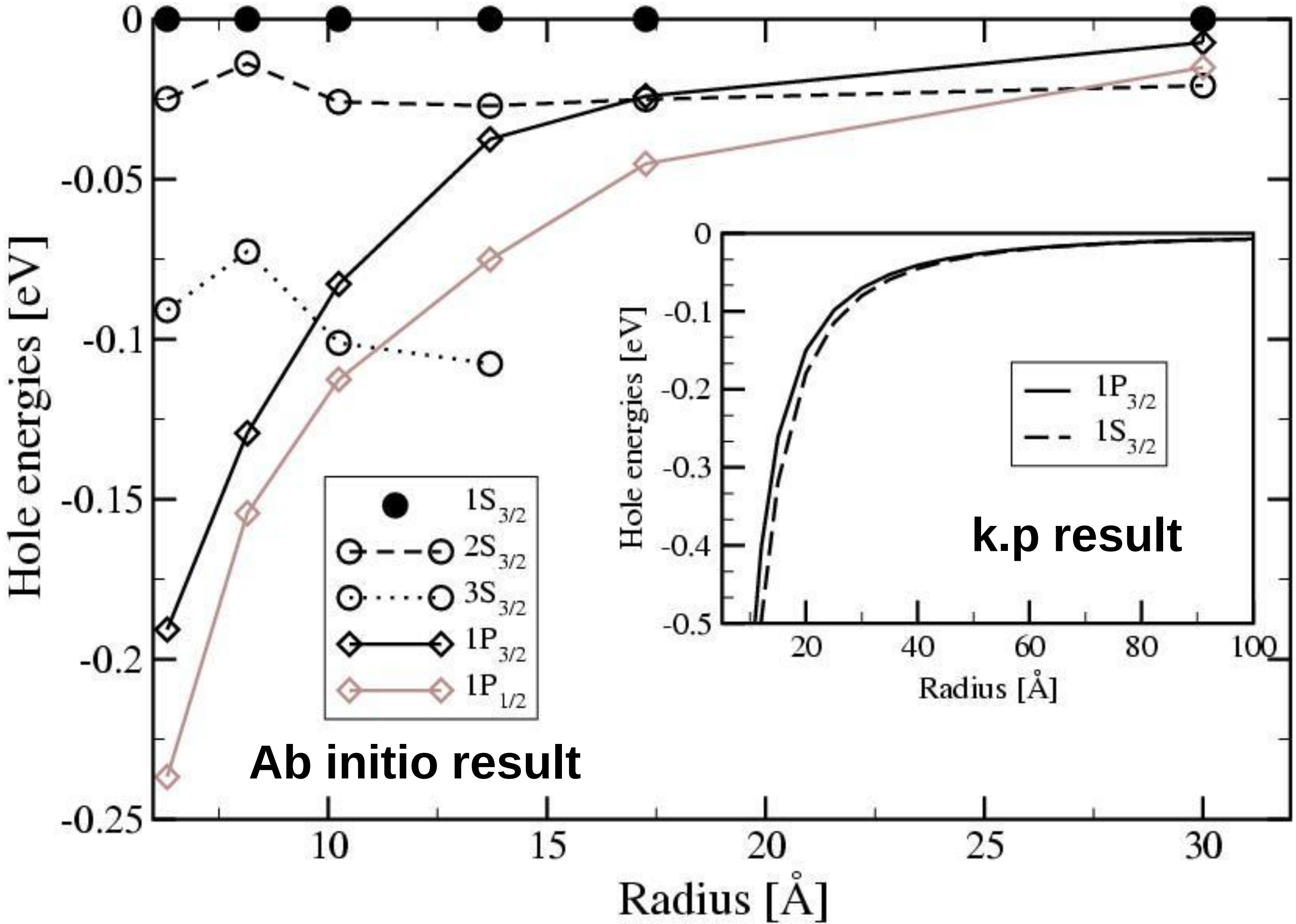


CdS quantum dot: p or s VBM exciton ?

Large experimental Stoke shift:

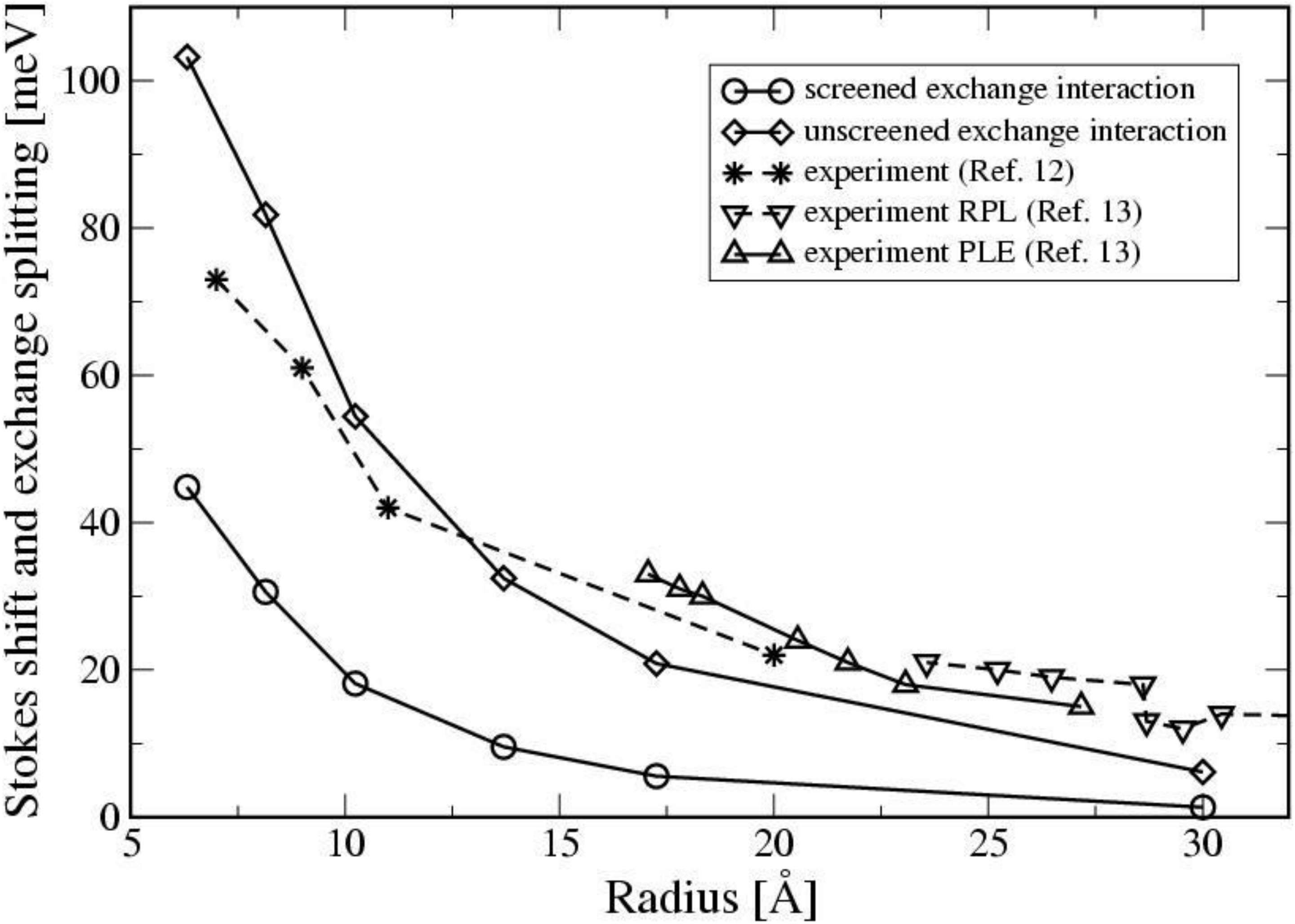
Due to: spin-forbidden dark exciton

or: spatial s-p forbidden dark exciton ?

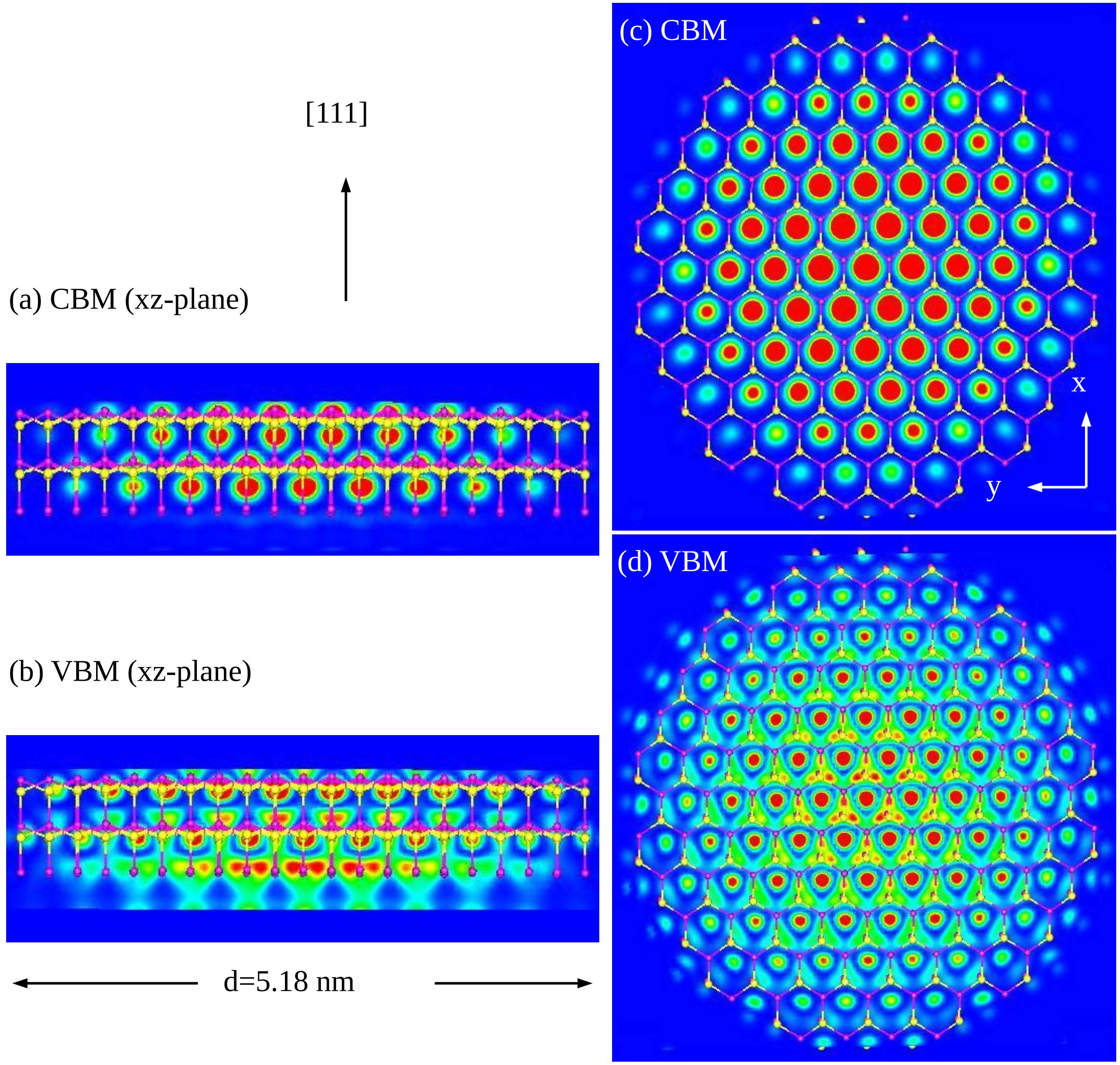


Exchange splitting caused of Stoke shift (CdS QD) ?

Should exchange splitting be screened ?
(Further experimental investigation will be helpful)

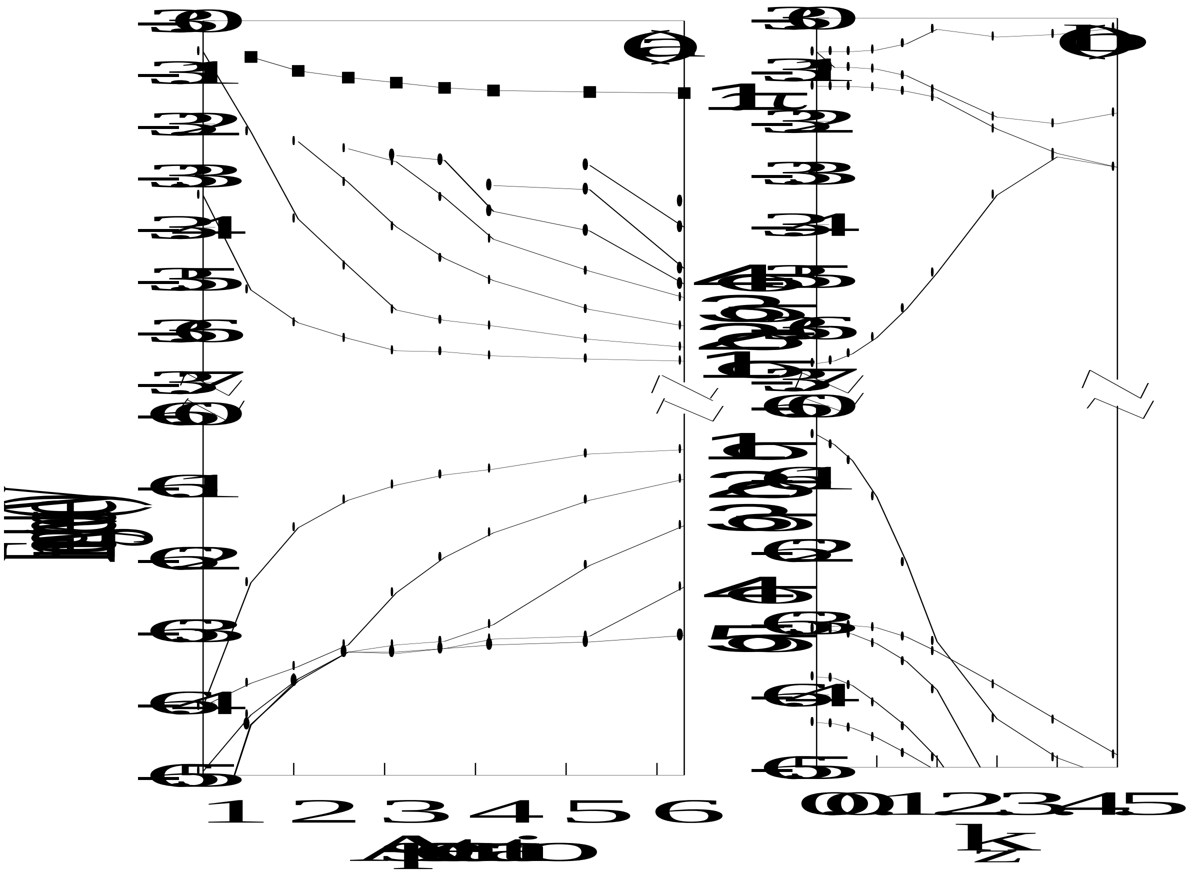


Quantum wire electronic states (InP)



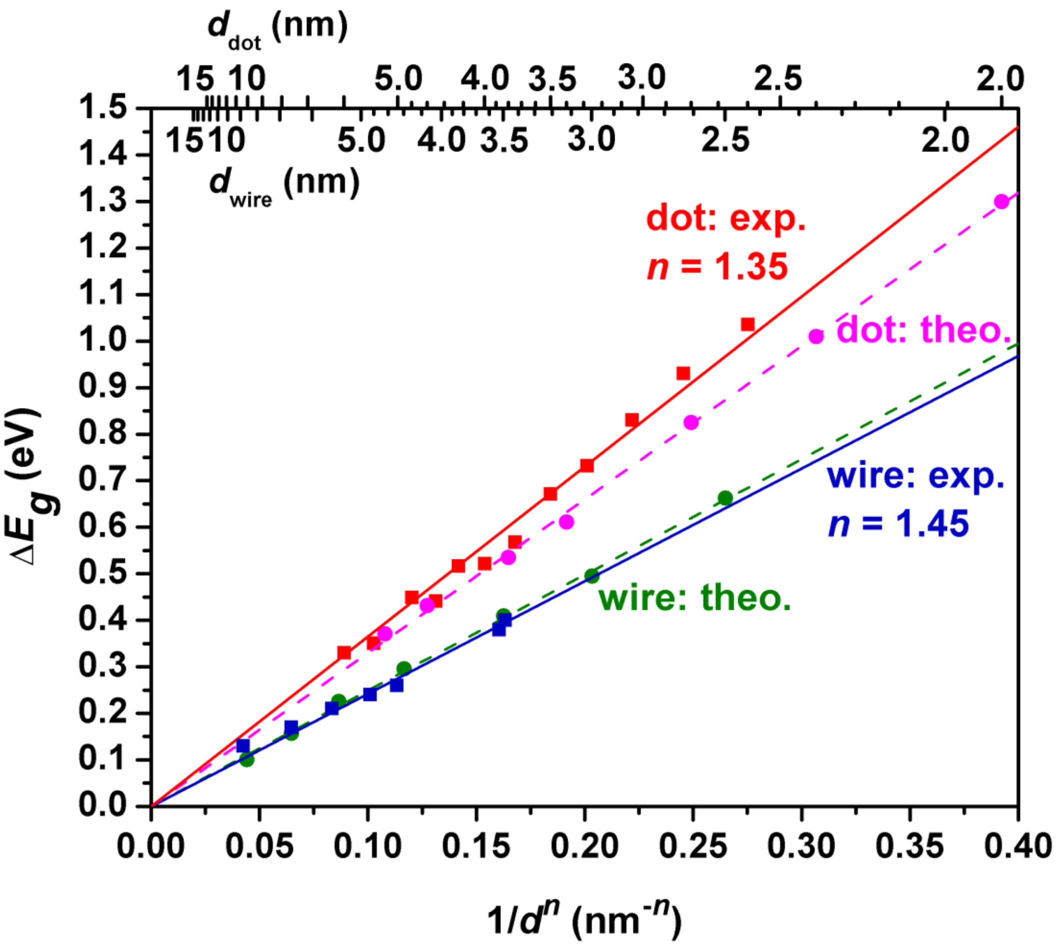
InP quantum rods and wires

(111) direction rods and wires

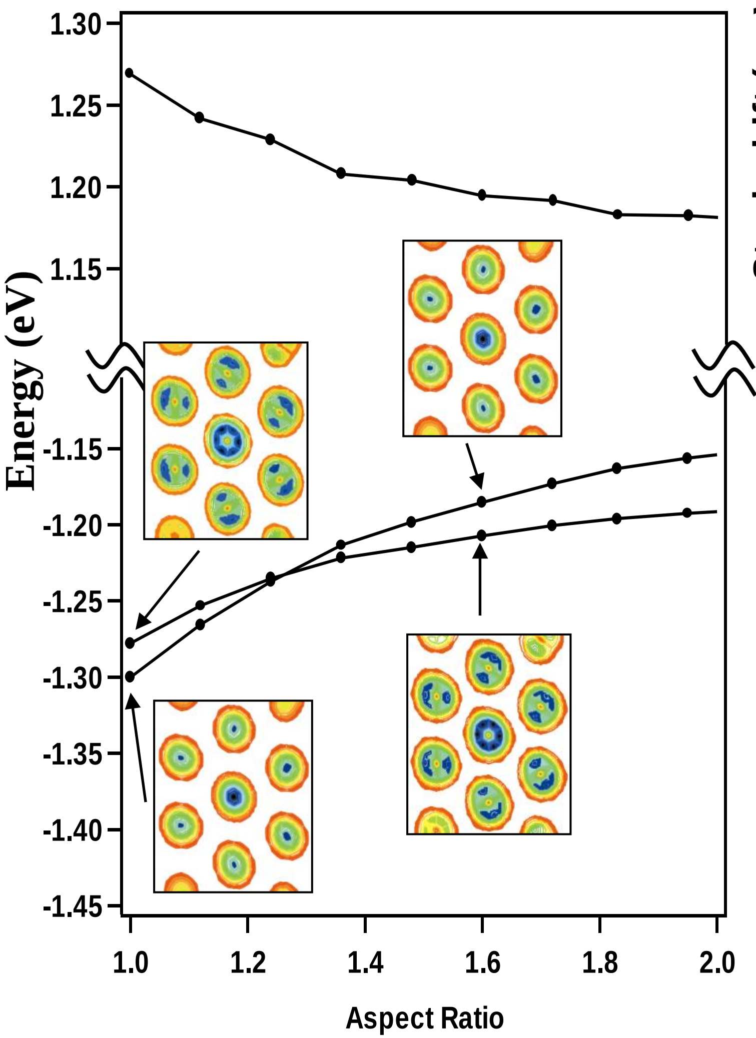


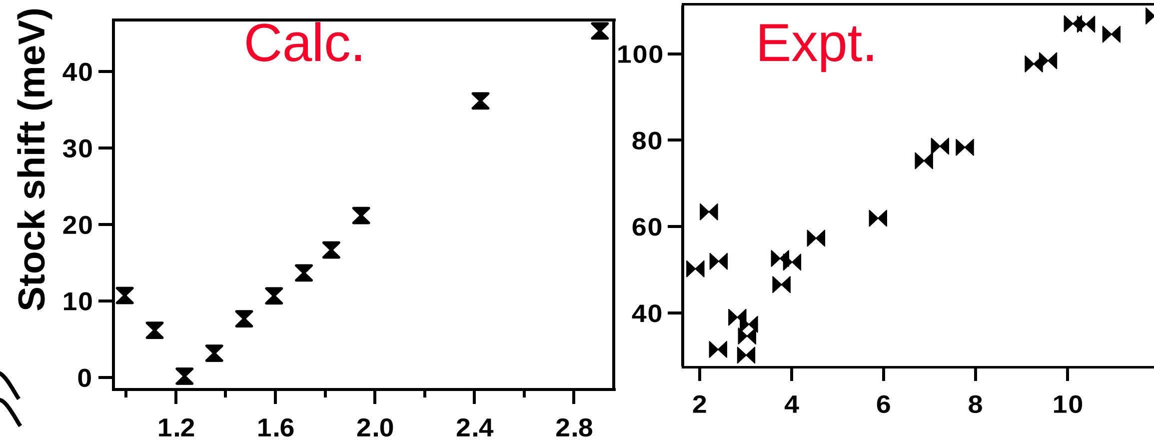
Rods Wire

InP wires / InP dots

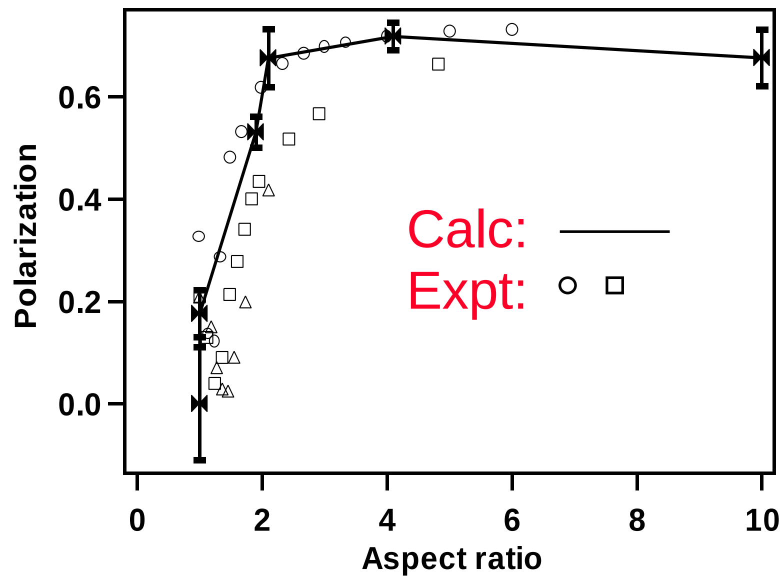


Polarization of quantum rods (CdSe)





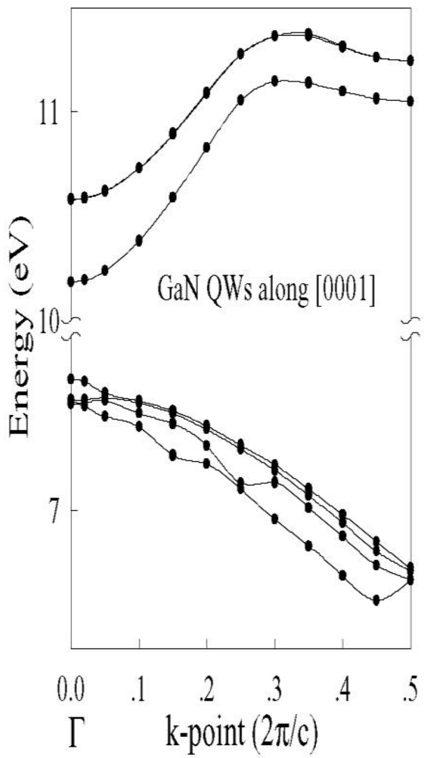
Aspect ratio of the quantum rods

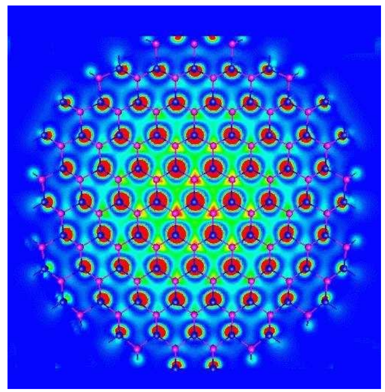


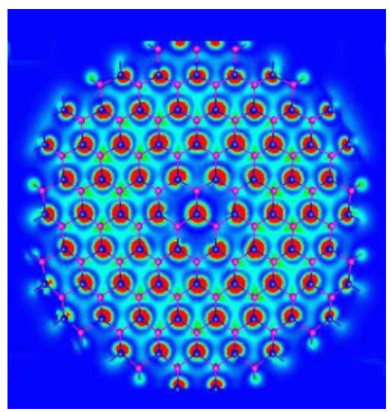
GaN (111) and (112) quantum wires (WZ)

(111) GaN wire

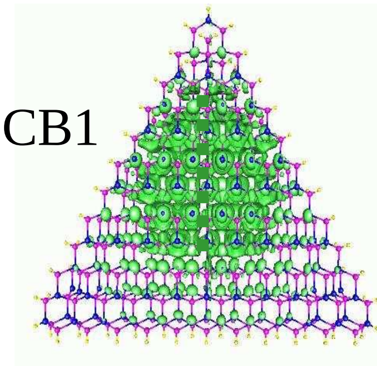
(112) GaN wire



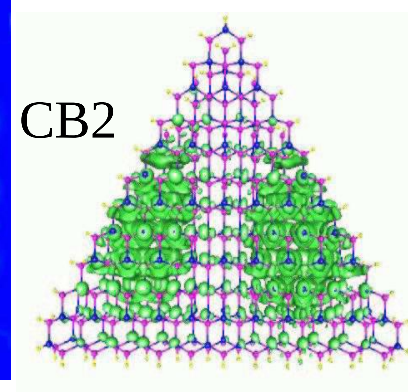


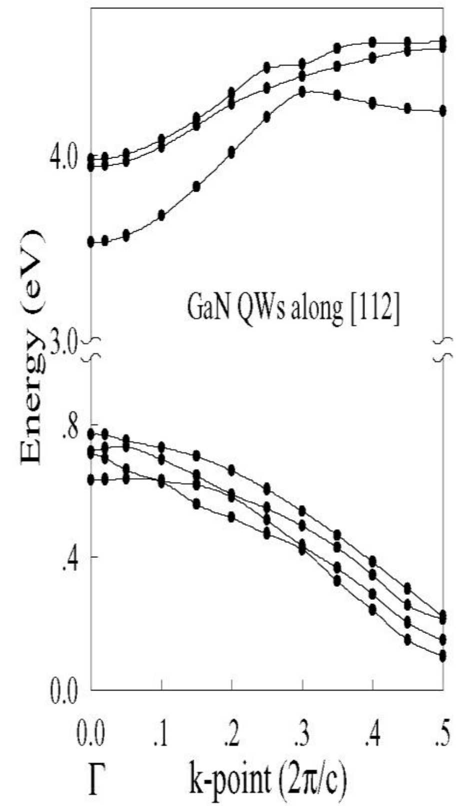


CB1

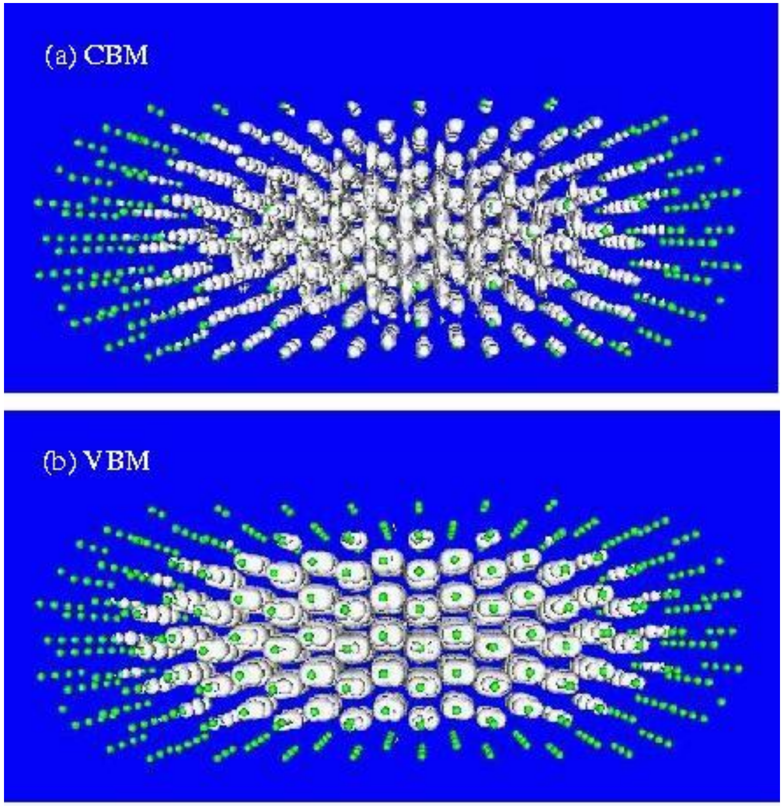


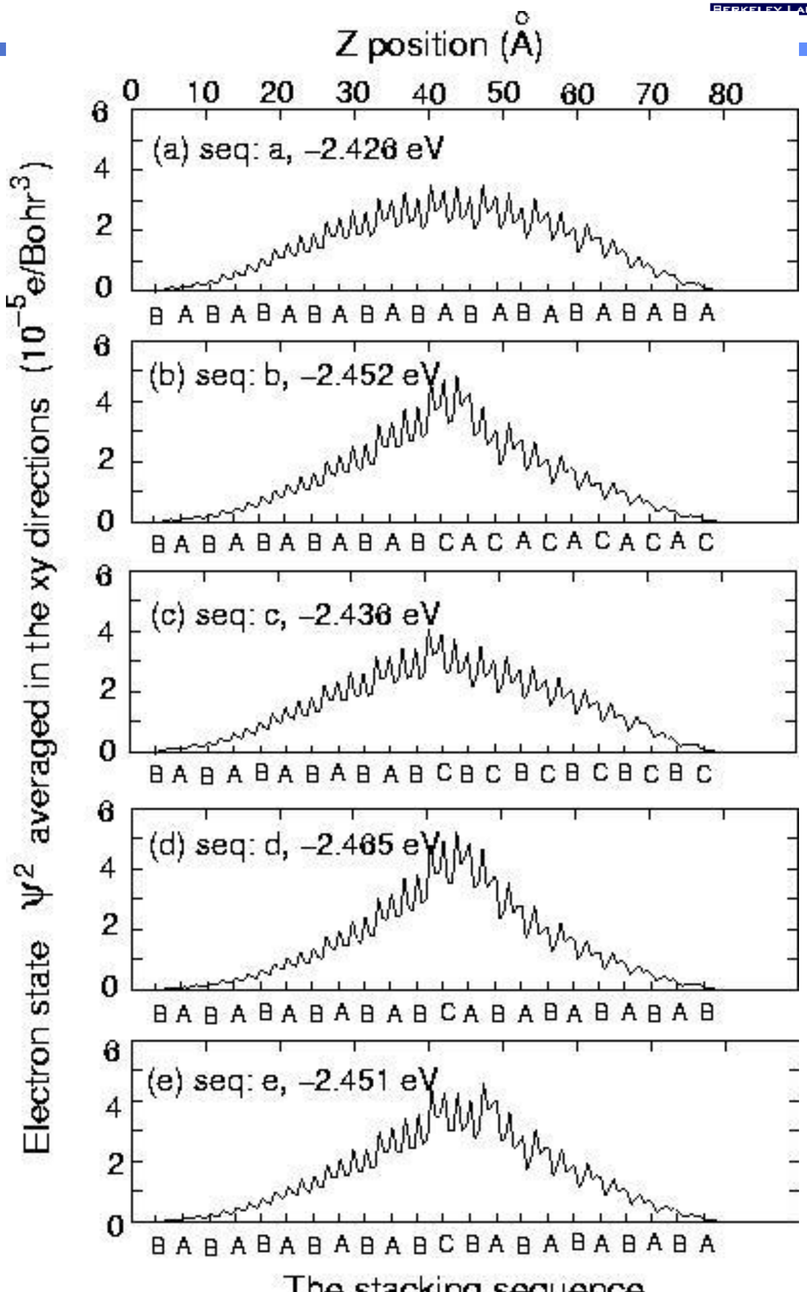
CB2





Effects of stacking faults





Bulged nanowires and their wavefunctions (CdSe)

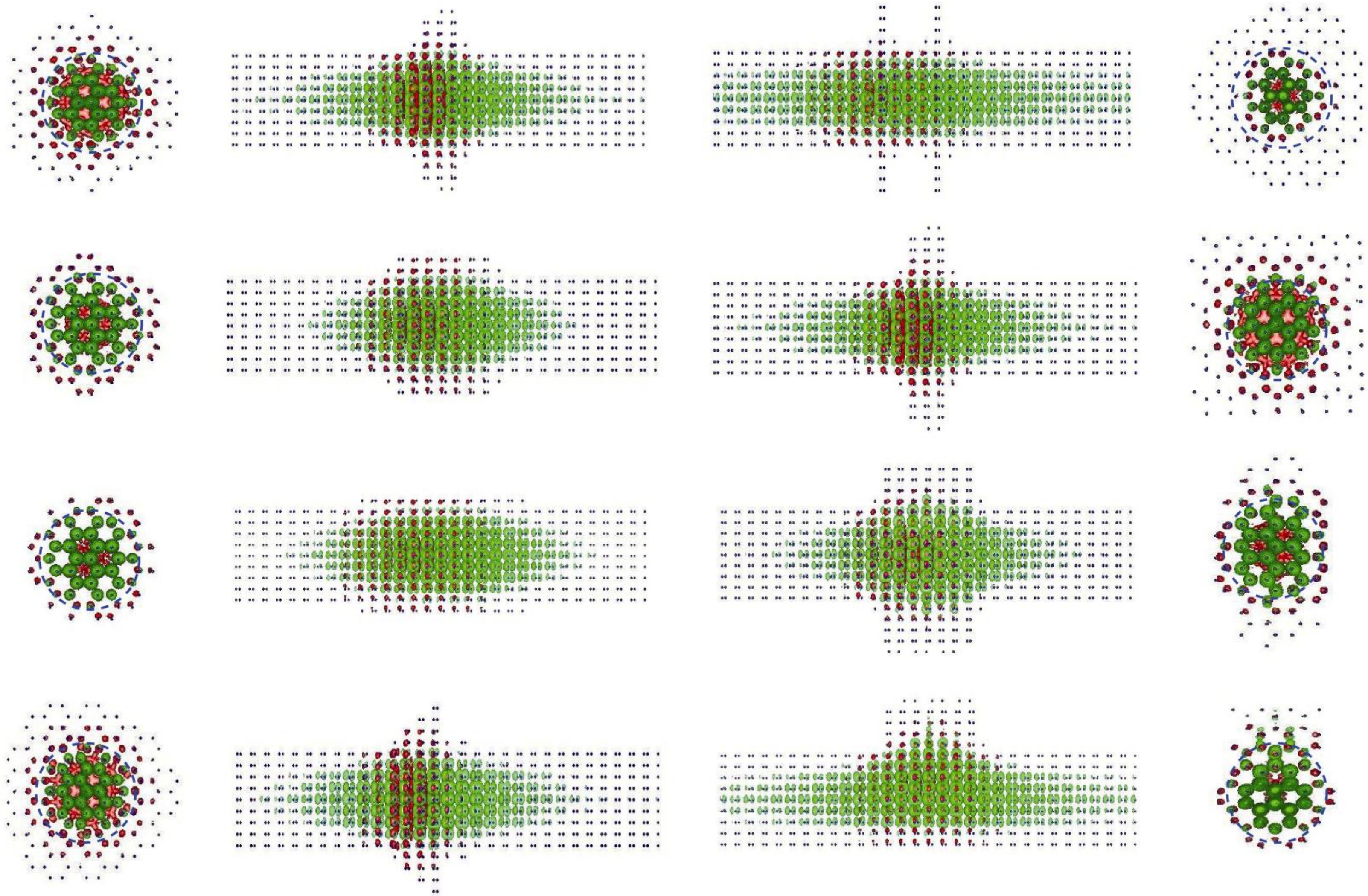
Green: VBM **Red: CBM** **CBM is more localized than VBM**

(1)

(2)

(3)

(4)



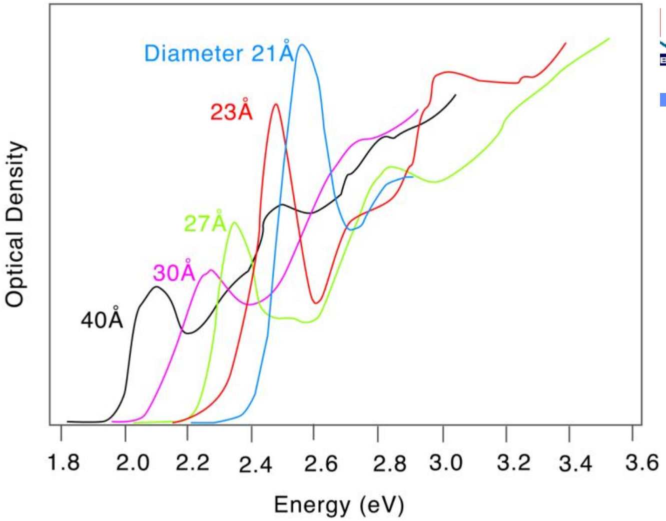
(5)

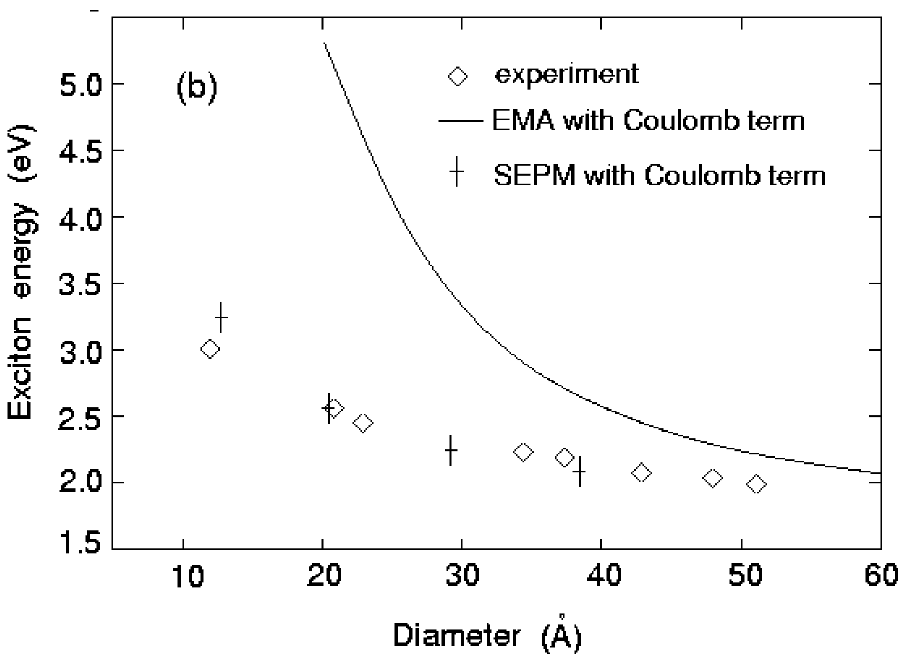
(6)

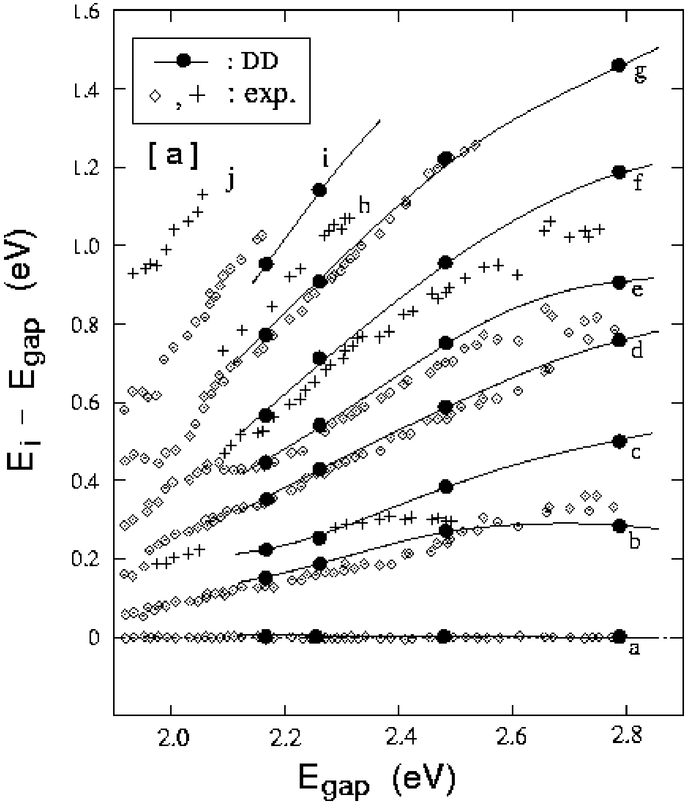
(7)

(8)

CdSe quantum dot results



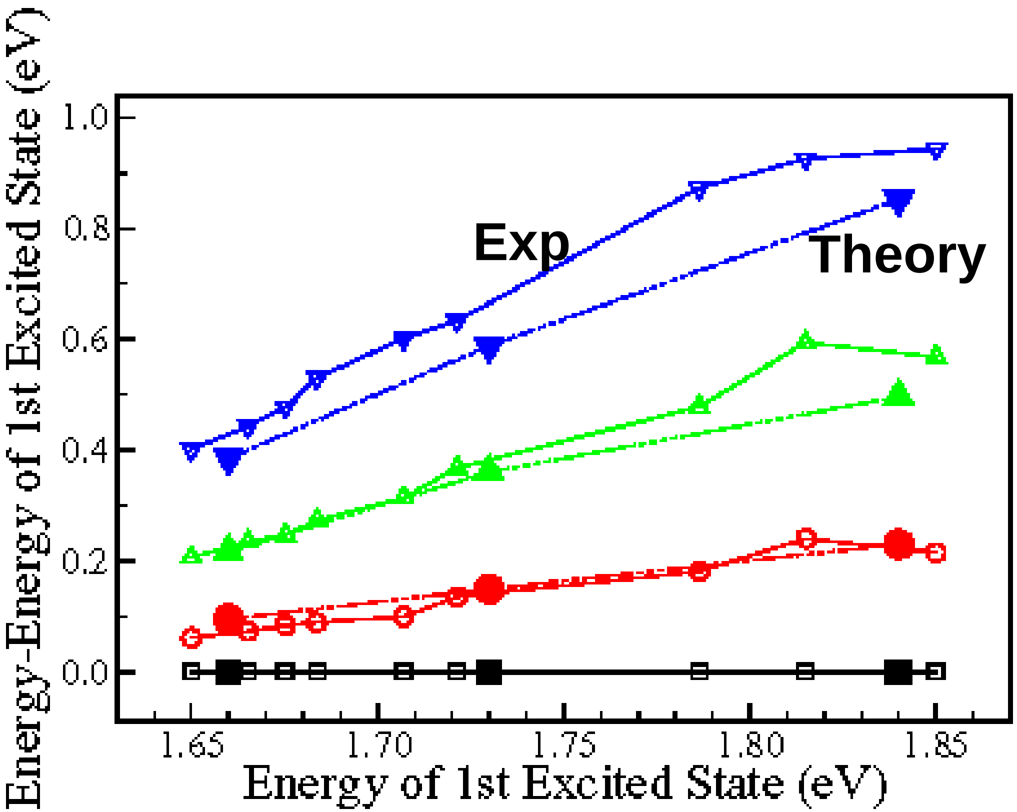


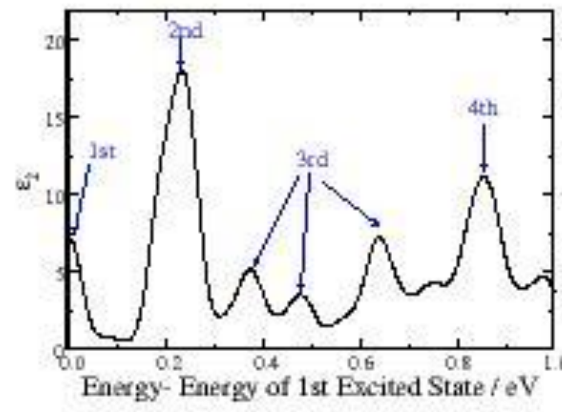


Office of Science
U.S. DEPARTMENT OF ENERGY

CdTe nanowire higher excited states

BERKELEY LAB





Calculated absorption spectrum

Ab initio quality charge patching method calculations (quantum wir diameters from 5 nm to 10 nm).

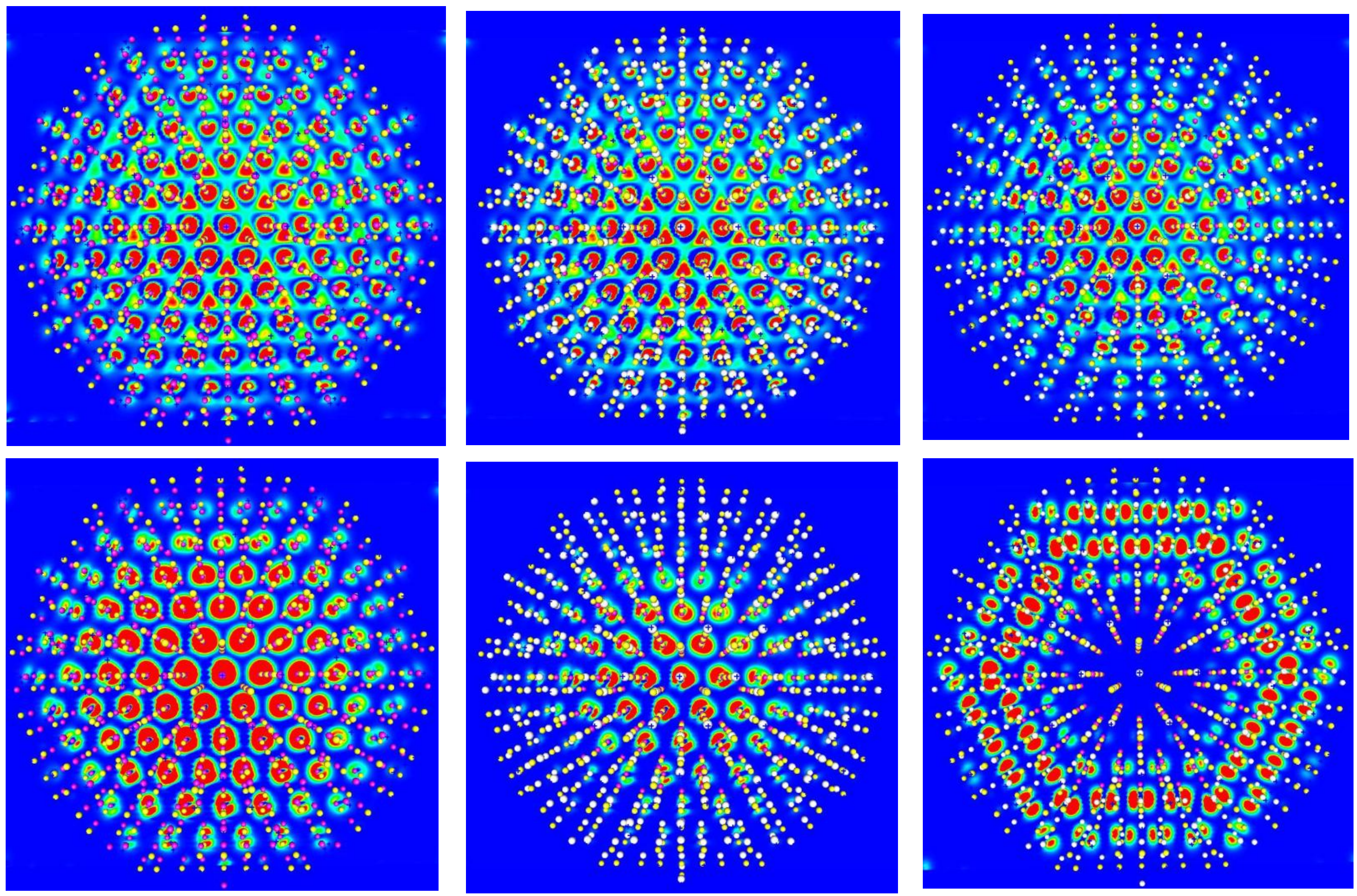
Experiment: Jianwei Sun, William E. Buhro, Washington Univ.

Core/shell quantum dots

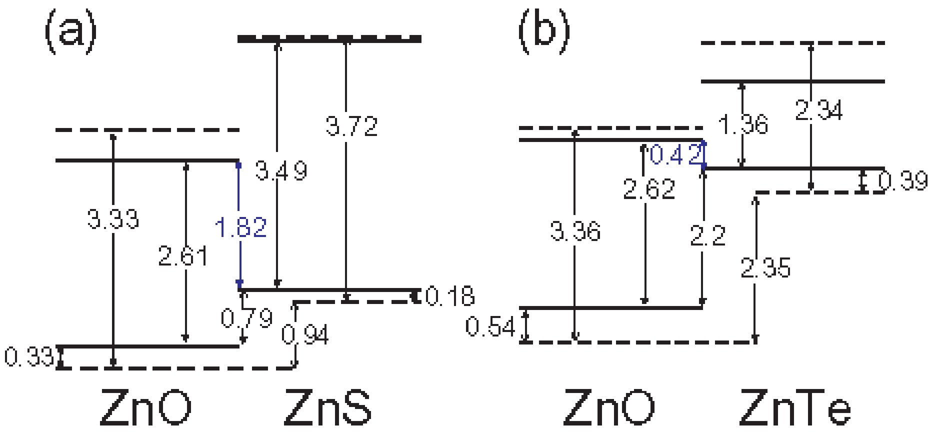
CdSe | CdSe/CdS | CdSe/CdTe

CBM

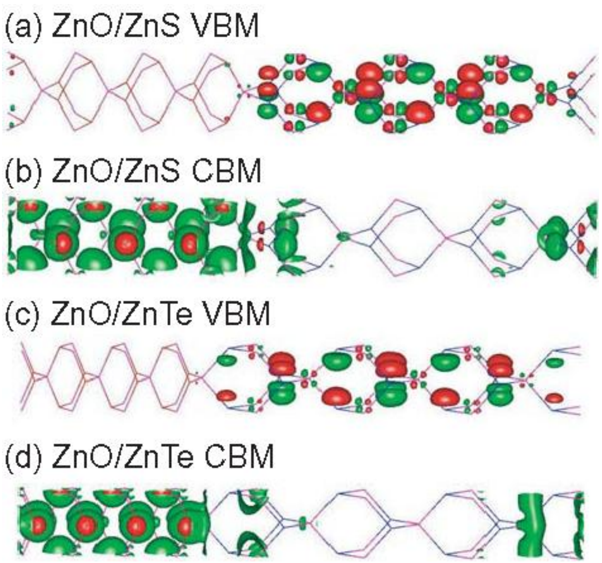
VBM

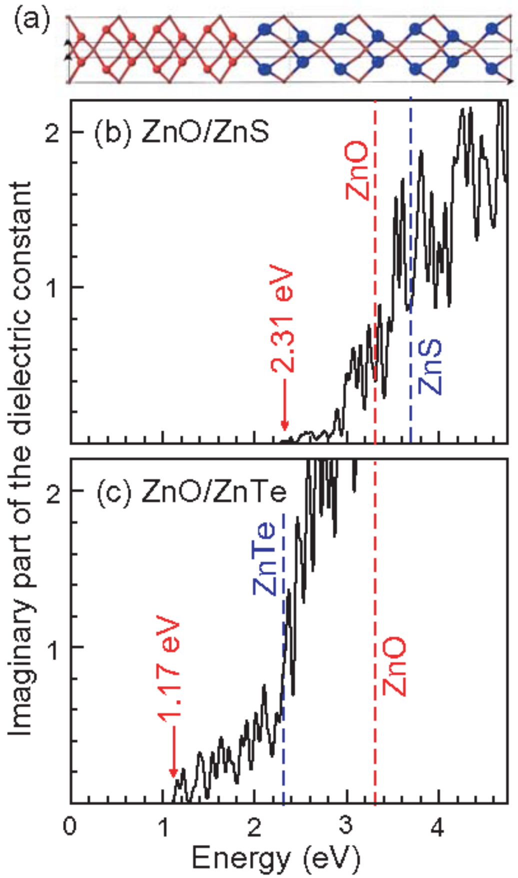


Solar cell using stable, abundant, and env. benign mat.



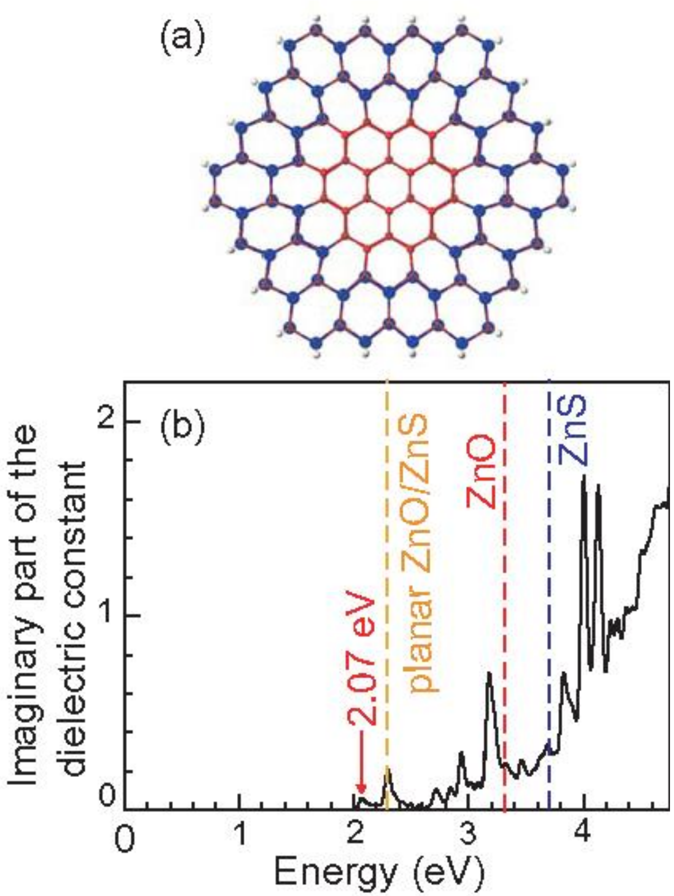
ZnO/ZnS, ZnO/ZnTe Superlattices



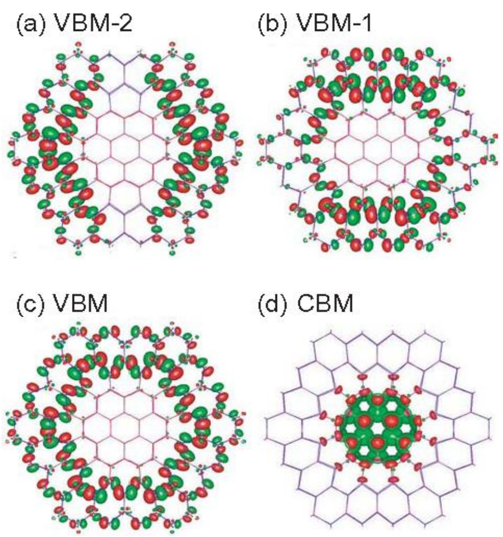


Solar cell using stable, abundant, and env. benign mat

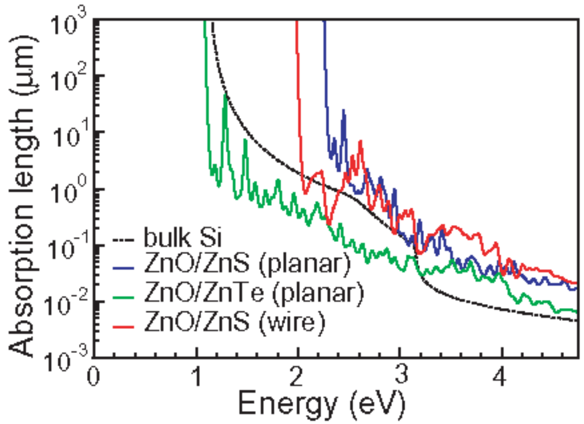
ZnO/ZnS core/shell wire



Band gap lowers down further from superlattices.

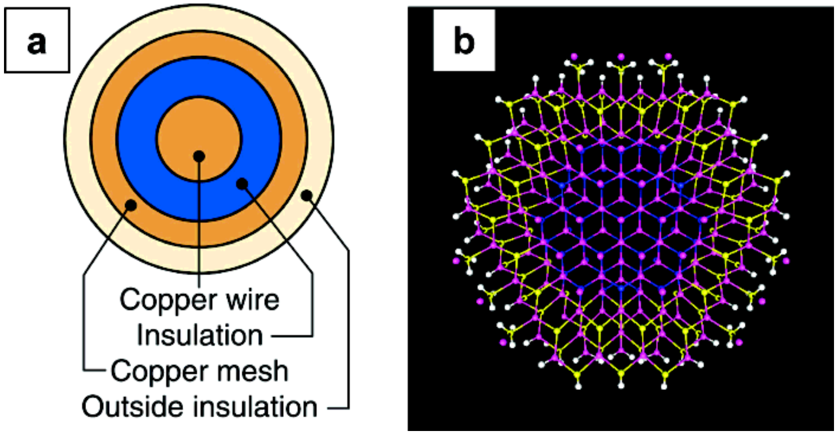


VBM-CBM transiton is forbidden due to state symmetry. This can prevent electron-hole recombination.

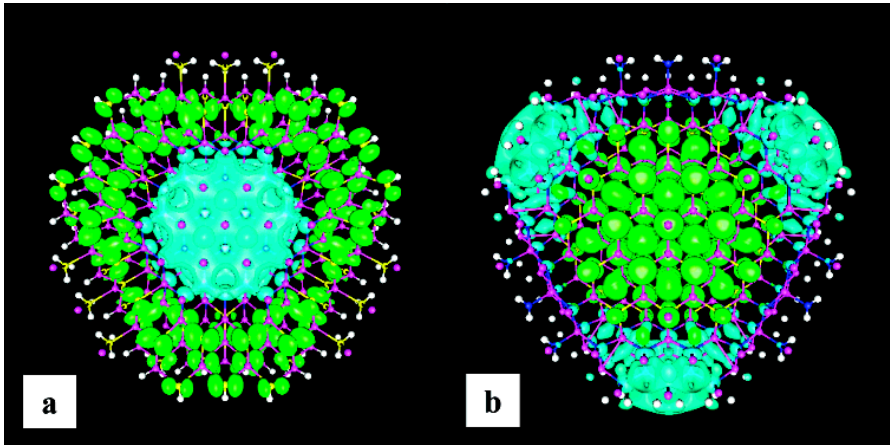


The absorption length is similar to bulk Si, thus similar among of material for solar cell.

Solar cell using core/shell wires of other materials



GaN/GaP core/shell nanowire

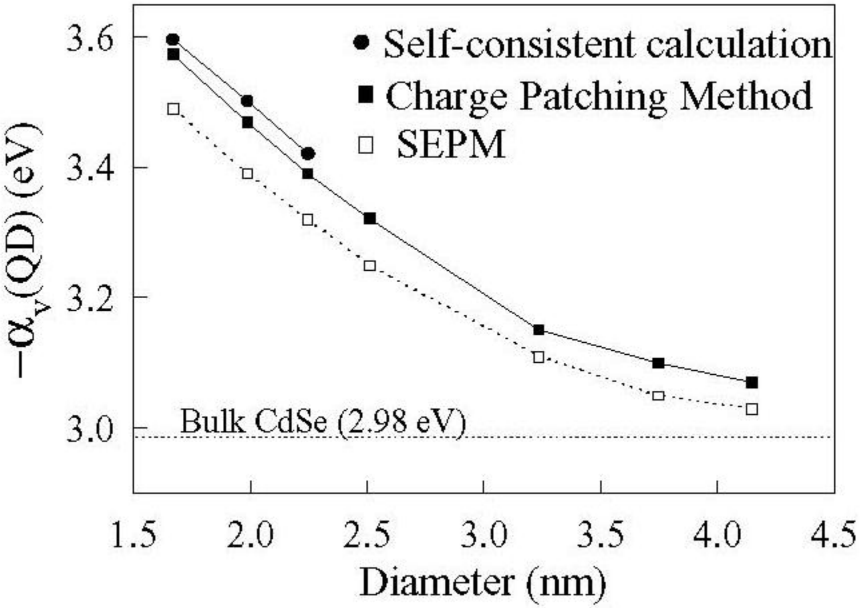


GaN (core)/GaP (shell) GaP (core)/GaN (shell)

Green: electron
Cyan: hole

Y. Zhang, L.W. Wang, A. Mascarenhas, Nanolett. 7, 1264 (2007).

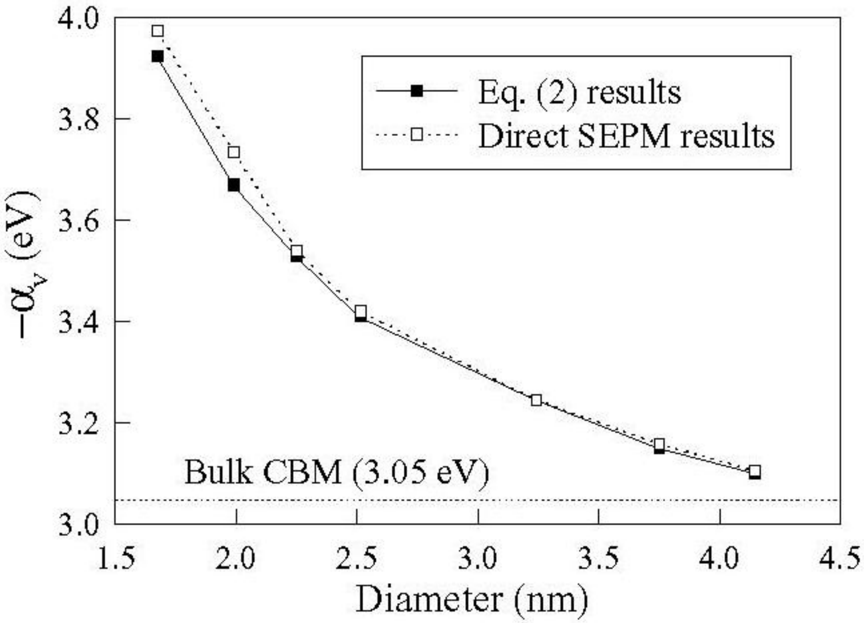
CdSe quantum dot optical pressure coeff.



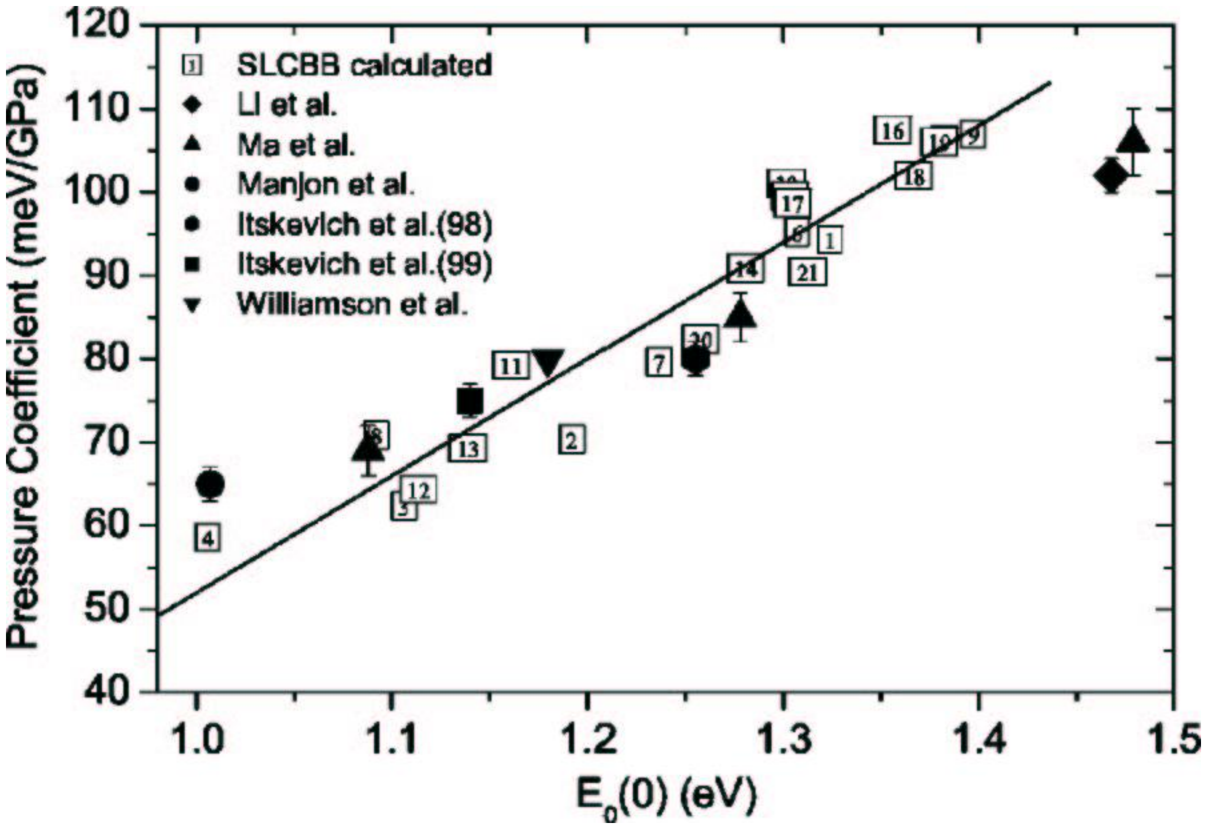
$$E_{CBM} = \sum_k W_k(k) E_c(k)$$ **Eq(1)**

$$\frac{dE_{CBM}}{d\ln V} = \sum_k \left[\frac{dW_c(k)}{d\ln V} E_c(k) + W_c(k) \frac{dE_c(k)}{d\ln V} \right]$$

Eq(2)



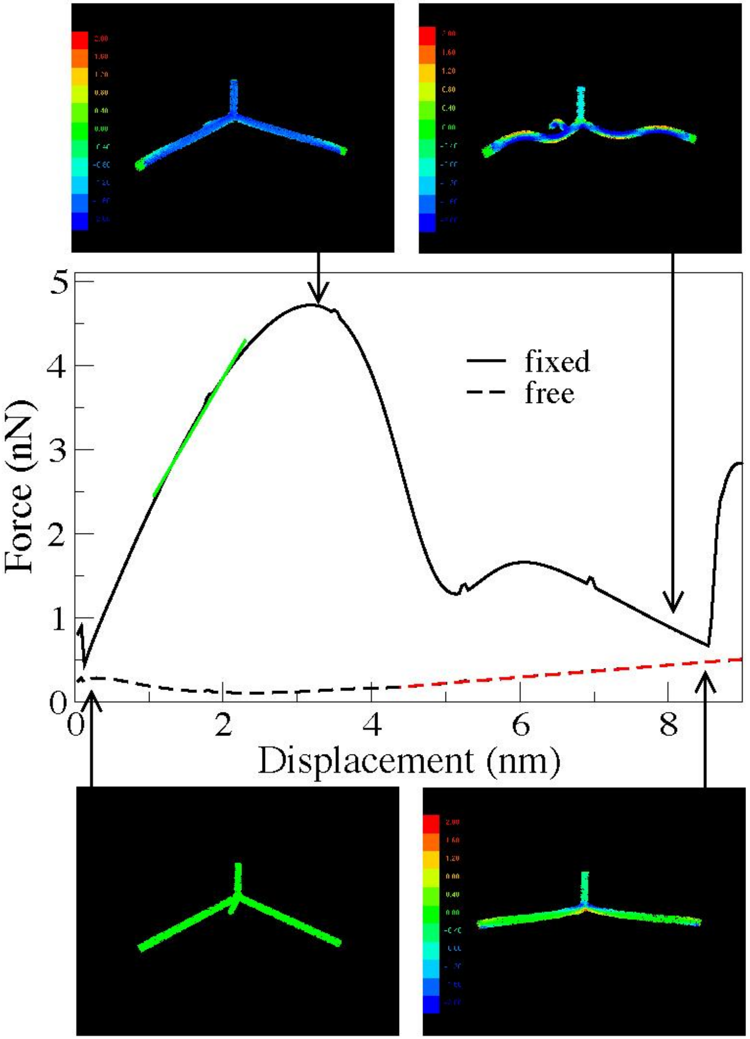
The calculated PC-Eg for InAs/GaAs QDs



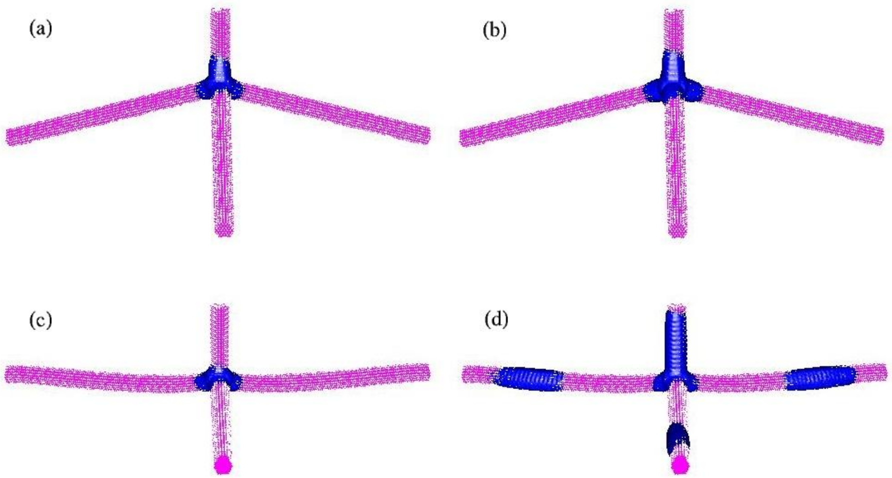
The black symbols are the experimental results, open squares are the calculated results

The PC change is due to nonlinear coefficient in InAs, and PC difference between InAs and GaAs.
Can use PC to determine the wavefunction localization.

CdSe tetrapod under pressure



VBM **CBM**

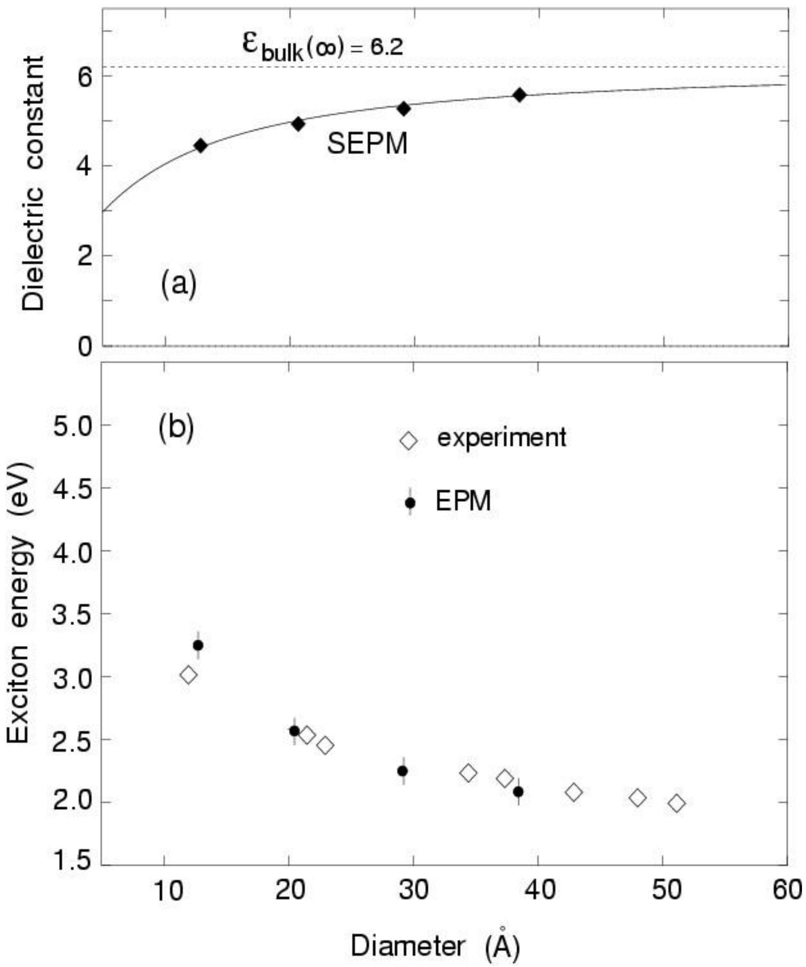


State crossing in CBM and PL change under uniaxial stress

Mechanical-optical effects

The average dielectric constant in a quantum dot

Theory



Wang, Zunger, PRB, 1996

Experiment

- **Using AFM tips**
- **Electrostatic force microscopy**
- **Measure the capacitance and ε**

Bulk ε = 6.2

Dot ε = 4.5 for d=5nm

Krauss and Brus, PRL, 1999

More perturbations

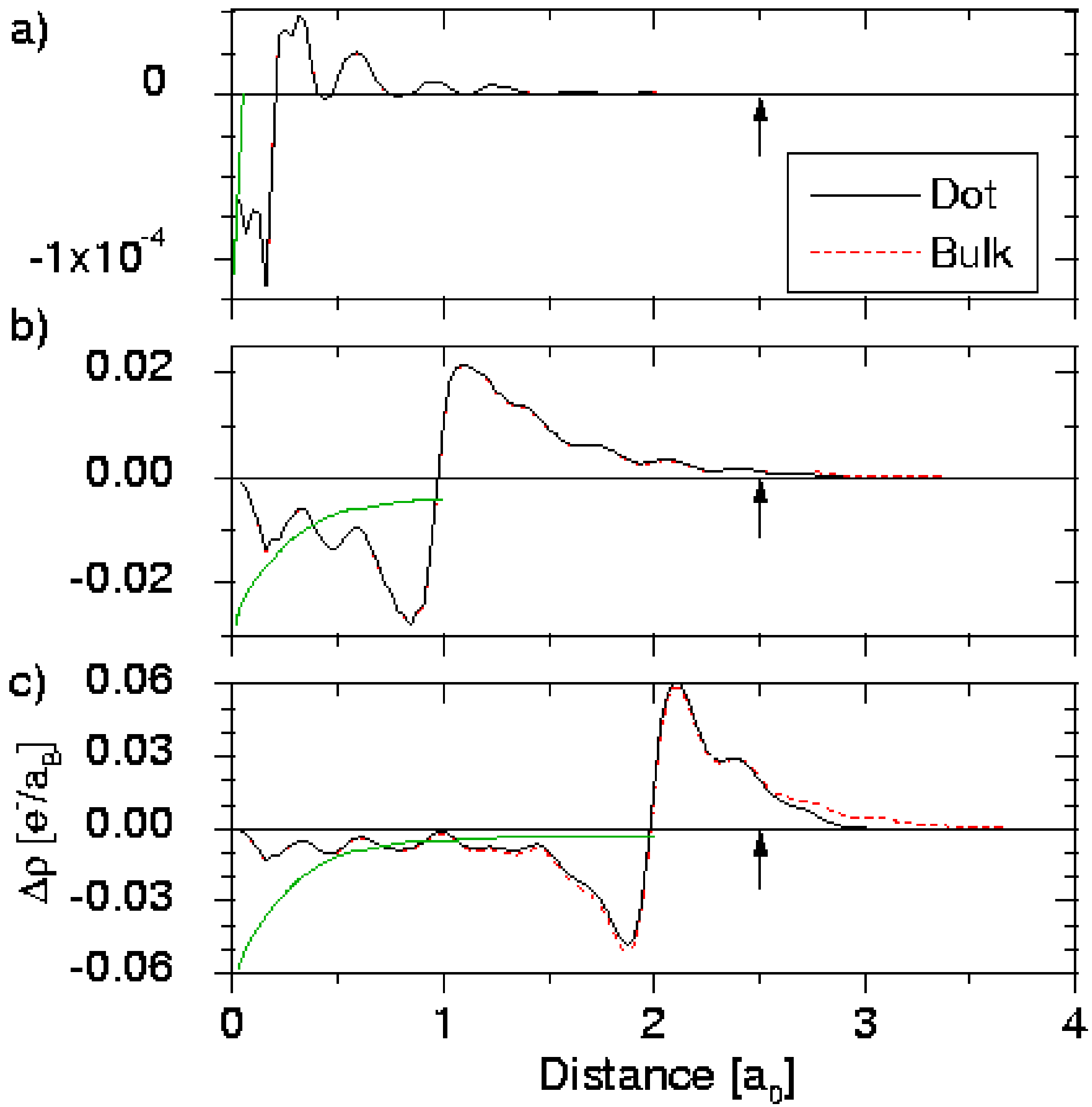
- **933-atom GaAs quantum dot**

- **Spherical average of the response charge**

- **More perturbations Coulomb like potentials**

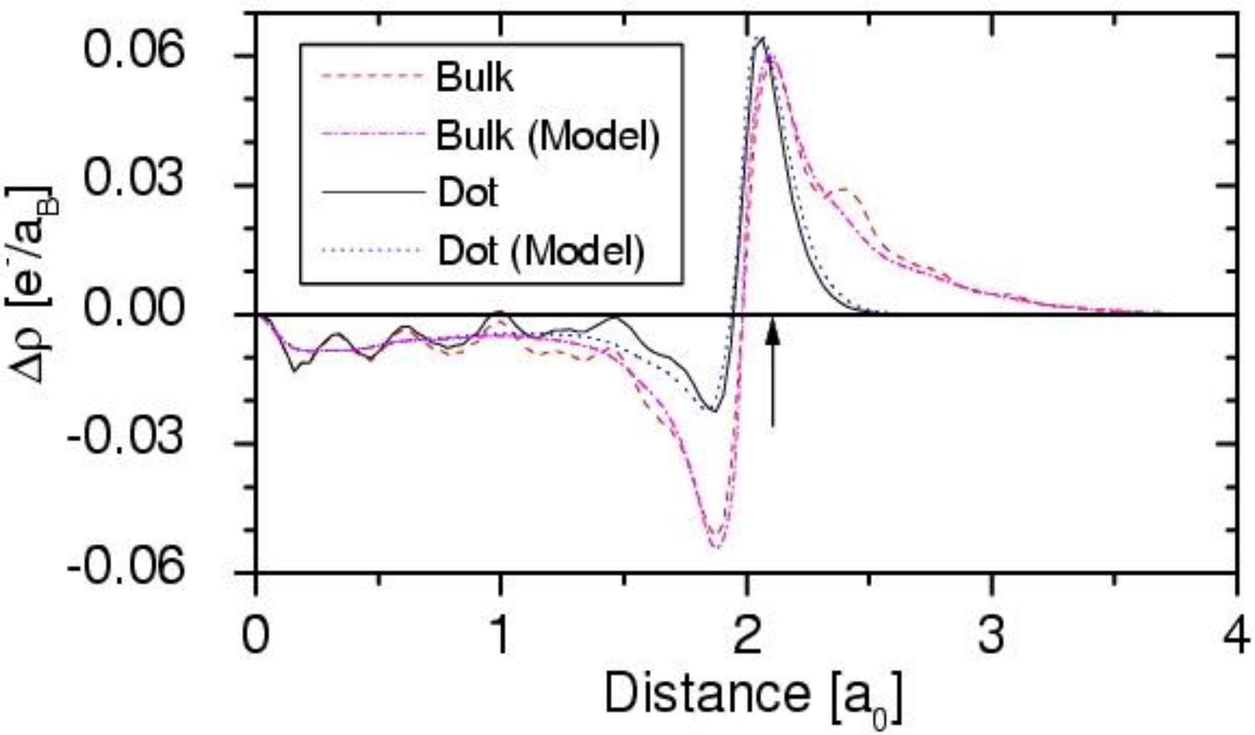
$$\delta V_{tot}(r) = \alpha / r \qquad \textbf{for } r < R_d$$

$$\delta V_{tot}(r) = 0 \qquad \textbf{for } r \rangle \; R_d$$



Testing the model (continued)

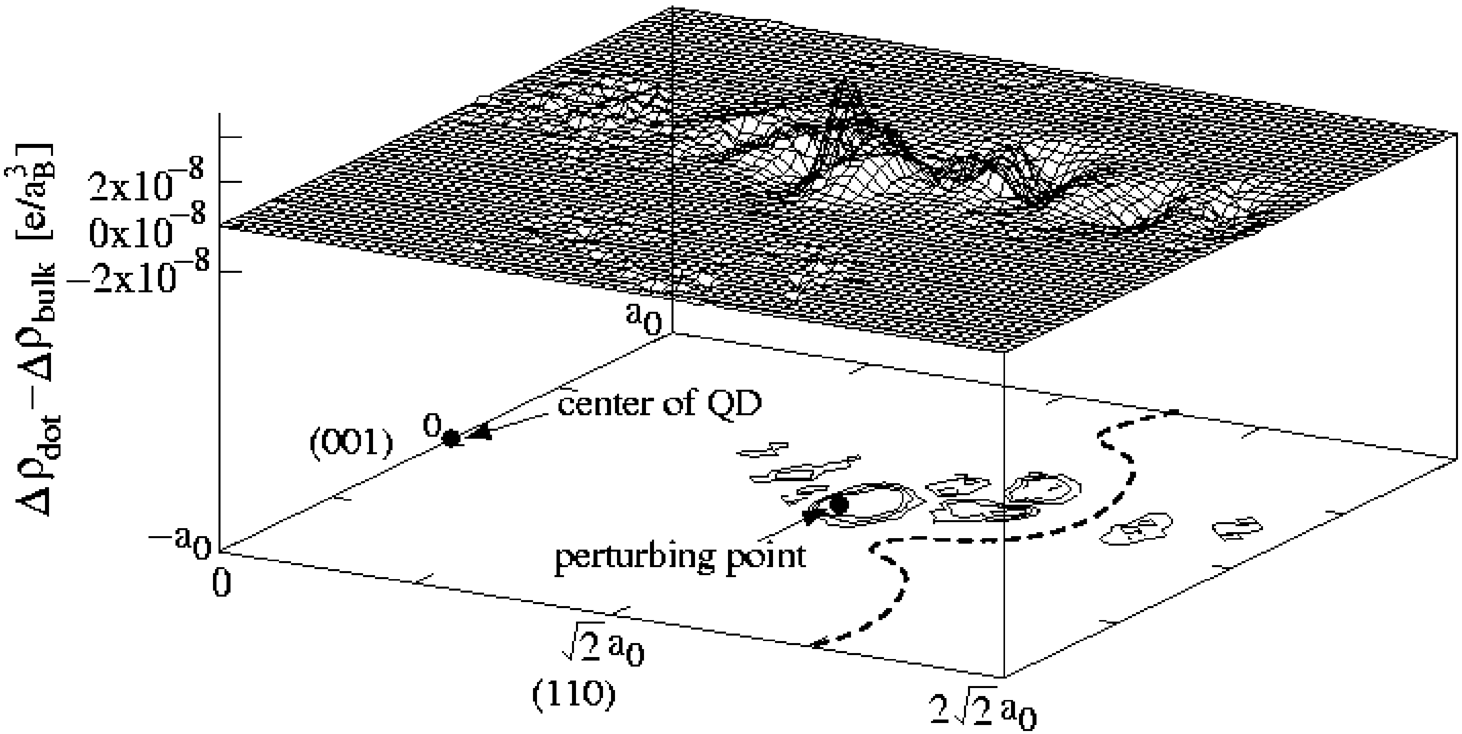
- Testing the model when both r_1,r_2 are close to the boundary.
- The bulk and dot response functions are significantly different.
- The Coulomb perturbation α/r truncated at $2a_0$, near the boundar
- 465-atom GaAs dot.



Average ε

	LDA	Model
465 dot	3.6	3.9
933 dot	4.6	4.3

Off center delta perturbation

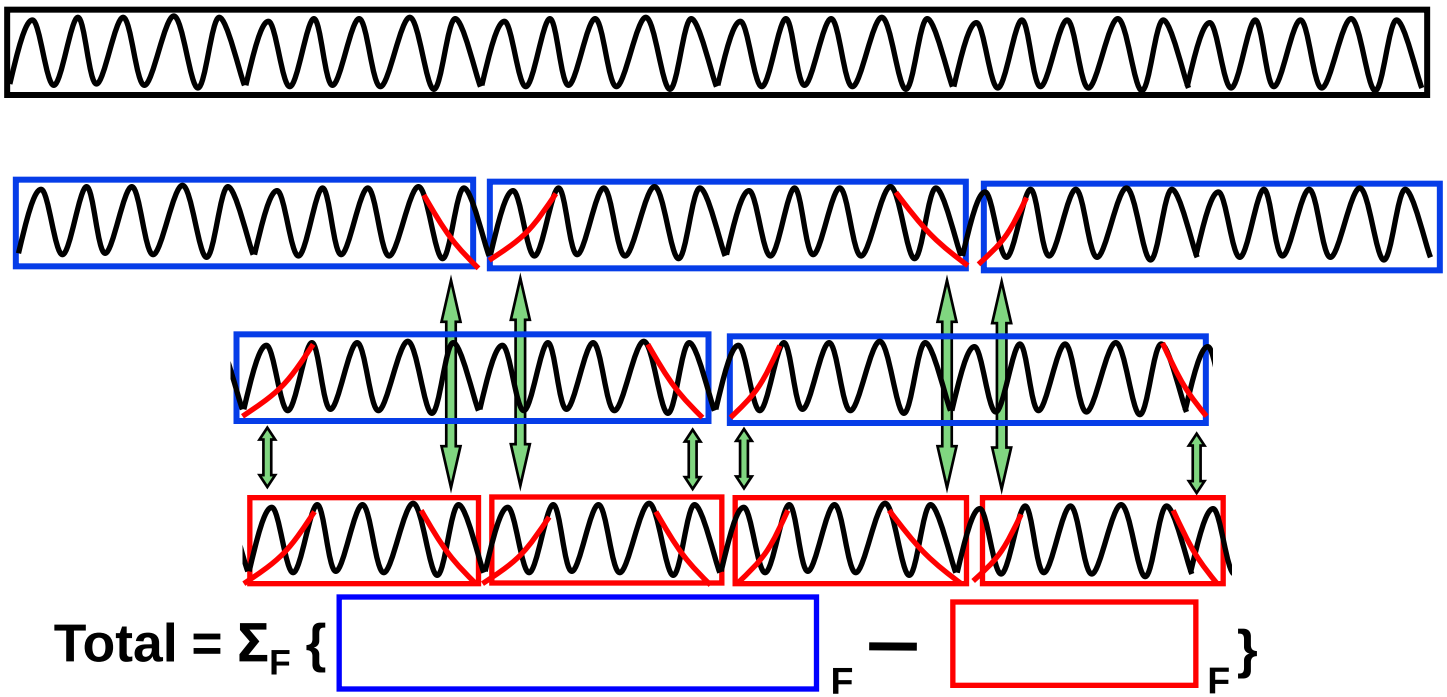


- **465-atom GaAs dot.**
- **only part of the [110] cross section is shown**
- **only the difference between dot and bulk response is shown.**

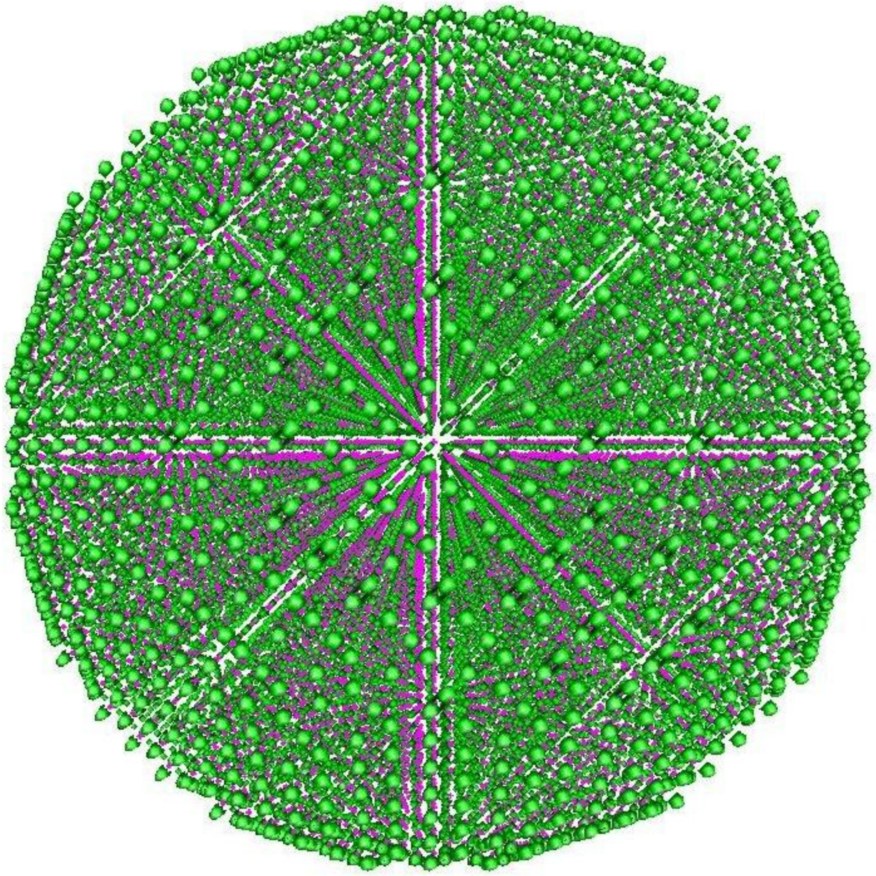
Linear scaling 3 dimensional fragment method (LS3DF)

- A novel scheme for dividing and patching the space
- No spatial partition functions
- Using overlapping positive and negative pieces (fragments)
- Cancellation for the artificial boundary effects

1D example:



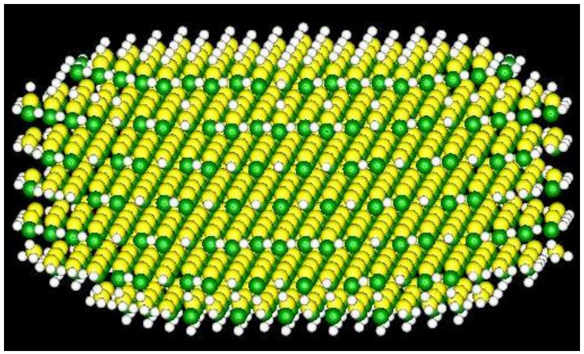
15,000 atom quantum dot: $Si_{13607}H_{2236}$



The charge density of a 15,000 atom Si quantum dot. It is calculated using 2048 processors, it takes about 5 hours. A direct LDA calculation would take a few months.

Geometric dependence of the total rod dipole moment

Using u=0.368, bulk formula P=0.043 (N_{Cd}+N_{Se}) (Debye), ε_{bulk}=7.466



R=7, L=3 (a.u.)

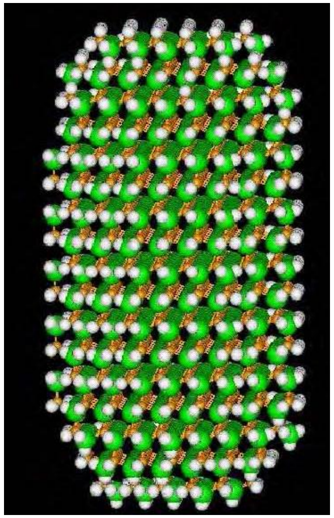
P=30.3 Debye

N_{Cd}=702
N_{Se}=702

ε_{dot}= 4.18
(calculated from continuous model)

P_{bulk}=20.08 Debye

$P_{dot}=P_{bulk}\ \varepsilon_{bulk}/\varepsilon_{dot}$
= 35.8 Debye



R=4.5, L=9 (a.u.)

P=73.3 Debye

N_{Cd}=714
N_{Se}=724

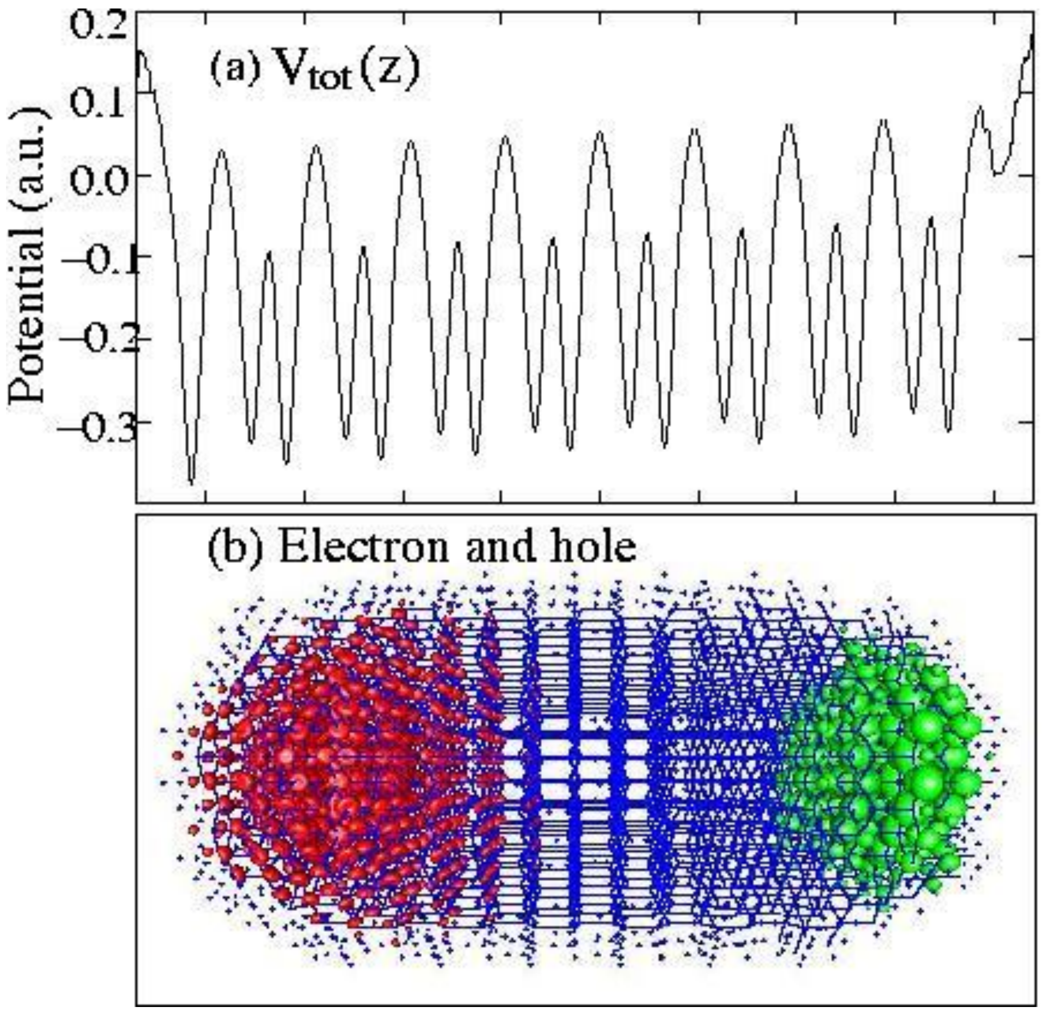
ε_{dot}= 2.17
(calculated from continuous model)

P_{bulk}=20.56 Debye

$P_{dot}=P_{bulk}\ \varepsilon_{bulk}/\varepsilon_{dot}$
= 70.8 Debye

The model: the total dipole moment is the screened dipole moment of an unscreened dipole contribution. While the unscreened dipole contribution depends only on volume, the efficiency of the screening depend on the dot geometry.

The possible effects of the dipole moment



$Cd_{714}Se_{724}$ WZ

CONCLUSIONS

- ❖ Charge patching method can be used to calculate nanocrystal electronic structures and optical properties with ab initio accuracy.

- ❖ Any semiconductor nanocrystals can be calculated with ideal surface passivations (in a few hours).

- ❖ Charge patching method can also be used to model the dielectric response of a nanocrystal.

- ❖ LS3DF method can be used to calculate >10,000 atom systems with total energy and forces.

Acknowledgement: Jingbo Li, Joshua Schrier, Byounghak Lee, Denis O. Demchenko, Zhengji Zhao.